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Version: Version of Record

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.21954/ou.ro.0000fcb0>

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Some Problems in Rigorous Equilibrium Statistical Mechanics.

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Date of submission: 14-3-78

Date of award: 20-7-78

Mathematical Physics

March, 1978.

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Abstract. In this dissertation we deal with some problems of classical statistical mechanics. In chapter 1 we review the problem of the thermodynamic equivalence of ensembles for equilibrium ensembles of classical statistical mechanics. We show how the problem of the thermodynamic equivalence of ensembles is solved with the help of generalized Legendre transforms (defined in Appendix A).

In chapter 2 we present some new results concerning the continuity of the thermodynamic limit temperature and the derivation of the Gibbs canonical distribution. For a classical system of interacting particles we prove, in the microcanonical ensemble formalism of statistical mechanics, that the thermodynamic limit inverse temperature, is a continuous function of the energy density. We also prove that the inverse temperature of a system approaches the thermodynamic limit inverse temperature as the volume of the system increases indefinitely. We also show that the probability distribution for a system of fixed size in thermal contact with a large system approaches the Gibbs canonical distribution as the size of the large system increases indefinitely, if the composite system is distributed microcanonically.

In chapter 3 we present a review of the duplicate variable method as a simple and useful tool for proving correlation inequalities for the Ising ferromagnet and other lattice systems. Roughly speaking, the method consists in expressing a product of correlation functions as an expectation of a suitable function over a larger space. New variables are introduced through a transformation that is usually orthogonal, chosen in such a way that the correlation inequality we set to prove appears explicitly.

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INTRODUCTION

In this dissertation we deal with some problems of rigorous statistical mechanics. In chapter 1 we discuss the problem of the thermodynamic equivalence of ensembles for the equilibrium ensembles of classical statistical mechanics. In chapter 2 we present some new results concerning the continuity of the thermodynamic limit temperature as a function of the energy density in the microcanonical ensemble formalism and the derivation of the Gibbs canonical distribution. This chapter was written in collaboration with Prof. O. Penrose and is being submitted for publication in the Journal Of Statistical Physics. Chapter 3 deals with correlation inequalities for the Ising ferromagnetic system and the duplicate variable method as a valuable tool for proving these correlation inequalities.

Chapters 1 and 2 emphasize the use of the properties of convex functions in proving rigorous results of classical statistical mechanics. In chapter 1 we show how the problem of the thermodynamic equivalence of ensembles is best solved with the help of generalized Legendre transforms of convex functions (defined in Appendix A). In chapter 2, using the properties of convex functions, we prove in the microcanonical ensemble formalism, that the thermodynamic limit inverse temperature, is a continuous function of the energy density. From this result it follows that the probability distribution for a system of fixed size in thermal contact with a large system approaches the Gibbs canonical distribution as the size of the large system increases indefinitely, if the composite system is distributed microcanonically.

The material of chapters 1 and 2 was partly motivated by the work

of Mazur and van der Linden⁽³⁸⁾. They found an asymptotic formula for the microcanonical partition function of a classical system of interacting particles. As a corollary they proved that the thermodynamic limit microcanonical entropy density is related to the thermodynamic limit canonical Helmholtz free energy density through the usual Legendre transform. However, they made an assumption about the number of possible phase transitions which seemed to us could not be rigorously justified. This led us, on the one hand to review the problem of the thermodynamic equivalence of ensembles of equilibrium statistical mechanics, and on the other, to try to improve their work by removing the assumption mentioned.

In chapter 3 we present a review of the duplicate variable method as a simple and useful tool for proving correlation inequalities for the Ising ferromagnet and other lattice systems. Roughly speaking, the method consists in expressing a product of correlation functions as an expectation of a suitable function over a larger space. New variables are introduced through a transformation that is usually orthogonal, chosen in such a way that the correlation inequality we set to prove appears explicitly.

I would like to thank my supervisor Prof. O. Penrose for his valuable help and suggestions. Financial support from the British Council and the National University of Mexico is also acknowledged.

CHAPTER 1. EQUIVALENCE OF ENSEMBLES IN CLASSICAL STATISTICAL MECHANICS

1. INTRODUCTION

Statistical mechanics relates the properties of macroscopic objects to the properties of the microscopic atoms making up these objects. Macroscopically, the state of the system is characterized by a small number of parameters such as temperature or density. Microscopically, the state of the system may be characterized by the positions and momenta of the N particles that make up the system.

One of the main aims of equilibrium statistical mechanics is to establish sufficient conditions on the microscopic interactions of the particles of a system composed of a great number of them, in order that the system exhibit thermodynamic behaviour. Obviously, these conditions should be as general as possible. That is, one of the main problems of the equilibrium statistical mechanics is proving a theorem that would say something like : given that the interactions between the particles of a system satisfy such and such conditions, the system exhibits thermodynamic behaviour. The other aim of equilibrium statistical mechanics is to establish the particular thermodynamic behaviour given particular microscopic interactions between the particles of the system.

The method by which statistical mechanics provides a macroscopic description is by identifying the macroscopic states with probability measures over the phase space of the system (the set of all possible microscopic states). The values of macroscopic parameters are then expectation values with respect to such measures of appropriate functions defined over the phase space.

The preferred probability measure is the microcanonical since it is the one most satisfactorily justified (through the ergodic hypothesis or the hypothesis of equal a priori probabilities). However, the canonical and grand canonical measures are the most widely used in calculations, although many others are also used ^(1,2,3).

In this and the next chapter we will discuss some of the difficulties encountered in the rigorous solution of the first problem mentioned above. In order to be able to speak unambiguously of a thermodynamic description of the system, it is necessary to perform what is known as "taking the thermodynamic limit", which means roughly speaking, to take as thermodynamic parameters of the system the limit, as the volume of the system increases indefinitely, of appropriate averages of phase functions. One expects that the thermodynamic descriptions obtained through any of the different ensemble measures will all be equivalent. To establish rigorously sufficient conditions under which all such thermodynamic descriptions are equivalent is the problem of the thermodynamic equivalence of ensembles, which we state in detail in section 2.

In section 3 we review the work that has been done on the subject, and in section 4 we present briefly the elegant solution given by Galgani, Manzoni and Scotti ⁽⁴⁾. Generalized Legendre transforms play a dominant role throughout the discussion. They are defined and their most important properties stated in Appendix A. In Appendix B we include a summary of thermodynamics which briefly exhibits the kind of structure that rigorous statistical mechanics attempts to explain.

2. STATEMENT OF THE PROBLEM

We are interested with the statistical mechanical description of a classical continuous system composed of particles of mass m having only translational degrees of freedom in a v -dimensional space. For each $N > 0$, the Hamiltonian

$$H(p_1, \dots, p_N, x_1, \dots, x_N) = \sum_{i=1}^N \frac{p_i^2}{2m} + U(x_1, \dots, x_N) \quad (1.1)$$

describes the microscopic dynamics. In this expression, $p_i \in \mathbb{R}^N$ and $x_i \in \mathbb{R}^N$ for $i = 1, \dots, N$ denote the momentum and position of the i th particle. U denotes the potential energy which is assumed not to depend on the momenta.

We define the microcanonical partition function $\Omega_\Lambda(E, N)$ ¹, the canonical partition function $Q_\Lambda(\beta, N)$ and the grand canonical partition function $\Xi_\Lambda(\beta, \mu)$ by

$$\Omega_\Lambda(E, N) = \frac{1}{N!} \int_{\mathbb{R}^N} dp_1 \dots dp_N \int_{\Lambda^N} dx_1 \dots dx_N \delta^{-} [H(p_1, \dots, p_N, x_1, \dots, x_N) - E] \quad (1.2)$$

$$\begin{aligned} Q_\Lambda(\beta, N) &= \frac{1}{N!} \int_{\mathbb{R}^N} dp_1 \dots dp_N \int_{\Lambda^N} dx_1 \dots dx_N \exp \left[-\beta H(p_1, \dots, p_N, x_1, \dots, x_N) \right] \\ &= \beta \int dE e^{-\beta E} \Omega_\Lambda(E, N) \end{aligned} \quad (1.3)$$

$$\Xi_\Lambda(\beta, \mu) = \sum_{N=0}^{\infty} \exp(-N\mu) Q_\Lambda(\beta, N). \quad (1.4)$$

-
1. There are other definitions of the microcanonical partition function. They all lead, as we will comment later, to equivalent thermodynamic descriptions.

The symbol E denotes the energy of the system, N the number of particles that form it and Λ the region in v -dimensional space it is enclosed in; β denotes the inverse temperature of the system and μ its chemical potential multiplied by $-\beta$. The symbol δ^- denotes the 1-unit step function.

We also define the functions $S_\Lambda = S_\Lambda(E, N)$, $\bar{F}_\Lambda = \bar{F}_\Lambda(\beta, N)$ and $\bar{p}_\Lambda = \bar{p}_\Lambda(\beta, \mu)$ by ²

$$S_\Lambda = S_\Lambda(E, N) = \log \Omega_\Lambda(E, N), \quad (1.5)$$

$$\bar{F}_\Lambda = \bar{F}_\Lambda(\beta, N) = -\beta^{-1} \log Q_\Lambda(\beta, N), \quad (1.6)$$

$$\bar{p}_\Lambda = \bar{p}_\Lambda(\beta, \mu) = \beta^{-1} v^{-1}(\Lambda) \log E_\Lambda(\beta, \mu), \quad (1.7)$$

where $v(\Lambda) = \int_\Lambda dx$.

Our first impulse is to identify S_Λ with the thermodynamic entropy, \bar{F}_Λ with the Helmholtz free energy and \bar{p}_Λ with the pressure as is done in introductory courses. However, ⁽⁵⁾"a very little study of the statistical properties of conservative systems of a finite number of degrees of freedom is sufficient to make it appear, more or less distinctly, that the general laws of thermodynamics are the limit towards which the exact laws of such systems approximate when their number of degrees of freedom is indefinitely increased." For example, the pressure cannot be defined as the partial derivative of S_Λ with respect to the volume, without specifying the shape of Λ and how it is altered. As suggested by Gibbs, letting Λ grow indefinitely along a reasonable sequence, we can get rid of the shape dependence of the functions defined above and then the limits of these functions can be

2. We choose units where Boltzmann's constant is 1.

rigorously identified as thermodynamic functions. As Lebowitz⁽⁶⁾, has pointed out, we have to resort to this limiting process not because we are interested in infinite systems as such, but because it is a rigorous way of considering physical situations in which shape and surface effects are unimportant. It turns out, also, to be the way in which phase transitions are introduced in the theory⁽⁷⁾.

The limiting process mentioned above is the problem of the thermodynamic limit and can be stated as follows: to find sufficient conditions on the potential U and to indicate a limiting process (which we denote by $\lim_{\Lambda \rightarrow \infty}$) under which it is possible to prove the existence and establish the properties of the functions $s = s(\epsilon, \rho)$, $f = f(\beta, \rho)$ and $p = p(\beta, \mu)$ defined by

$$s = s(\epsilon, \rho) = \lim_{\Lambda \rightarrow \infty} V^{-1}(\Lambda) s_{\Lambda}(E, N) \quad (1.8)$$

$$f = f(\beta, \rho) = \lim_{\Lambda \rightarrow \infty} V^{-1}(\Lambda) F_{\Lambda}(\beta, N) \quad (1.9)$$

and

$$p = p(\beta, \mu) = \lim_{\Lambda \rightarrow \infty} p_{\Lambda}(\beta, \mu) \quad (1.10)$$

where

$$\epsilon = \lim_{\Lambda \rightarrow \infty} E V^{-1}(\Lambda) \text{ and } \rho = \lim_{\Lambda \rightarrow \infty} N V^{-1}(\Lambda).$$

In expression (1.9) $F_{\Lambda}(\beta, N)$ is defined by $F_{\Lambda} = -\beta \bar{F}_{\Lambda}$ and in expression (1.10) $p_{\Lambda}(\beta, \mu)$ is defined by $p_{\Lambda} = \beta \bar{p}_{\Lambda}$. Then $s = s(\epsilon, \rho)$ will be identified with the entropy density of the system, $f = f(\beta, \rho)$ with the Helmholtz free energy density multiplied by $-\beta$, and $p = p(\beta, \mu)$ with the pressure multiplied by β .³

-
3. This is the problem of the thermodynamic limit for the microcanonical, canonical and grand canonical ensemble formalisms. Obviously, similar problems exist for all the other equilibrium ensembles of classical statistical mechanics.

If one succeeds in establishing, under the same conditions on the potential U and by the same limiting process, the existence and properties of $s = s(\epsilon, \rho)$, $f = f(\beta, \rho)$ and $p = p(\beta, \mu)$, one arrives at three independent thermodynamic descriptions, so there still remains to be proved that they are equivalent. This, precisely, is the problem of the thermodynamic equivalence of ensembles. Since $s = s(\epsilon, \rho)$, $p = p(\beta, \mu)$ and $f = f(\beta, \rho)$ are to be identified as fundamental relations (see Appendix B), the problem of the thermodynamic equivalence of ensembles will be solved if we succeed in proving that these functions are related by the appropriate generalized Legendre transforms. That is, we have to prove that (see Appendix B)

$$f = f(\beta, \rho) = \sup_{\epsilon} (s(\epsilon, \rho) - \beta \epsilon), \quad (1.11)$$

$$\begin{aligned} p = p(\beta, \mu) &= \inf_{\rho} \inf_{\epsilon} (\mu \rho + \beta \epsilon - s(\epsilon, \rho)) \\ &= \sup_{\rho} (f(\beta, \rho) - \mu \rho), \end{aligned} \quad (1.12)$$

hold. As we will see, the problem of the thermodynamic limit for the different ensembles and the problem of equivalence of ensembles are closely linked and are most satisfactorily solved at the same time.

3. THERMODYNAMIC EQUIVALENCE OF ENSEMBLES.

Although the need for going to the limit of an infinite system had been already recognized by Gibbs as far back as 1902, it was van Hove⁽⁸⁾, almost fifty years later, that first treated the problem rigorously. Even then, many people questioned the need for such a proof. van Hove tried to prove the existence of the thermodynamic limit function $f = f(\beta, \rho)$, under the assumptions that the particles interact through pair potentials with hard cores that fall off rapidly as the distance increases. The limiting process used in his proof was such that the fraction of volume of Λ lying within a fixed distance of the boundary of Λ tended to zero as Λ grew indefinitely. However, van Kampen pointed out a mistake in his proof (private communication to M. Fisher⁽⁹⁾). Yang and Lee⁽¹⁰⁾, proved the existence of the thermodynamic limit function $p = p(\beta, \mu)$ for hard core two body interactions with a finite range. Part of their proof is similar to the one of van Hove. These papers, however, did not consider the problem of the thermodynamic equivalence of ensembles. The results of Yang and Lee were later extended to the pressure ensemble⁽¹¹⁾.

Lewis⁽¹²⁾ in what appears to be the first paper that openly recognizes the problem of the thermodynamic equivalence of ensembles, proved the equality of the canonical and grand canonical pressures. The method of proof was later taken up by Ruelle⁽¹³⁾, and Fisher⁽⁹⁾, to prove the thermodynamic equivalence of the canonical and grand canonical ensemble formalisms.

The problem of the thermodynamic limit did not receive much attention until Ruelle⁽¹³⁾ solved the problem for the canonical and grand canonical ensembles. In his proof, he only considers pair

potentials, but removes the hard core condition. He imposes two conditions on the potential, the first implies that the potential is stable, which means that there exists a positive constant B such that $U(x_1, \dots, x_N) \geq -NB$. The second condition is that the two-body potential be attractive at long distances. The main result of Ruelle's paper is the following:

Let $\{N_i\}_{1 \leq i \leq \infty}$ be a sequence of positive integers such that $N_i \rightarrow \infty$ and $\{\Lambda_i\}_{1 \leq i \leq \infty}$ a sequence of cubes that grows indefinitely in such a way that $V(\Lambda_i) \rightarrow \infty$, where $V(\Lambda_i)$ denotes the volume of the cube Λ_i , and such that $V(\Lambda_i)/N_i \rightarrow v > v_{cp}$ ⁴. Let

$$\psi_{\Lambda_i}(\beta, N_i) = \frac{1}{N_i} \log Q_{\Lambda_i}(\beta, N_i)$$

and

$$p_{\Lambda_i}(\beta, \mu) = \frac{1}{V(\Lambda_i)} \log E_{\Lambda_i}(\beta, \mu). \quad (1.13)$$

Then

(i) There exists a function ψ such that

$$\psi(\beta, v) = \lim_{i \rightarrow \infty} \psi_{\Lambda_i}(\beta, N_i).$$

(ii) There exists a function p such that

$$p(\beta, \mu) = \lim_{i \rightarrow \infty} p_{\Lambda_i}(\beta, \mu) = \max_{0 < v < +\infty} \left(\frac{\psi(\beta, v) - \mu}{v} \right).$$

The main idea behind the proof consists in showing that the sequence $\{\psi_{\Lambda_i}(\beta, N_i)\}_{1 \leq i \leq \infty}$ is monotone decreasing and bounded below. The lower bound is found simply by inserting the stability condition

4. v denotes the specific volume ; if there are hard cores, v_{cp} is the close packing specific volume due to them. It can happen that $v_{cp} = 0$.

$U(x_1, \dots, x_N) \geq -NB$ in eqn.(1.3), while the proof that the sequence is monotonous follows from the second condition imposed on the potential. The proof of (ii) consists in using the conditions imposed on the potential U and the fact that the convergence of the sequence $\{\psi_{\Lambda_i}(\beta, N_i)\}$ is uniform on the compact subsets of the domain of ψ to prove that (for suitable values of N) $\exp(-\mu N)Q_{\Lambda}(\beta, N)$ approaches $[\mu - \psi(\beta, v)]/v$ and that only the maximum term in the argument of the logarithm function of eqn.(1.13) survives in the passage to the limit. However, the proof is valid only for cubes and does not consider more general shapes and to establish (ii) above it is assumed without proof that ψ is a twice differentiable function of the specific volume v .

Fisher⁽⁹⁾, using similar methods to those of Ruelle⁽¹³⁾, proved the existence of the thermodynamic limit Helmholtz free energy density and that it is a convex function of the number density ρ . The conditions under which the proof holds are very general, so general, that they haven't been improved on since. These conditions are:

- (a) The potential U is stable.
- (b) The potential U is tempered. If $W_{N_1 N_2}(x'_1, \dots, x'_{N_1}, x''_1, \dots, x''_{N_2})$ is the energy of interaction between a group of N_1 particles and a group of N_2 particles, the potential is tempered if there exists a $\lambda > 0$, $R_0 > 0$, $A \geq 0$ such that

$$W_{N_1 N_2}(x'_1, \dots, x'_{N_1}, x''_1, \dots, x''_{N_2}) \leq A_{N_1 N_2} r^{-\lambda}, \quad (1.14)$$

whenever $|x''_j - x'_i| \geq r \geq R_0$ for all $i = 1, \dots, N_1, j = 1, \dots, N_2$.

The temperedness condition provides an upper bound on the interaction energy between two groups of particles sufficiently far away from each other. Note that it is not

required that the potential U be a sum of 2-body interaction potentials.

- (c) The limiting process $\Lambda \rightarrow \infty$ is restricted to shapes where the surface does not grow too rapidly. (For the exact definition see Fisher's paper or ref.No.13,p.14).

Using the result of the thermodynamic limit for the free energy density, Fisher proves that the grand canonical thermodynamic limit exists and that it leads to the same results as the canonical, i.e., that (1.12) holds. The essential idea of the proof comes from recognizing that if Λ is sufficiently large, the grand partition function $E_{\Lambda}(\beta, \mu)$ defined by eqn.(1.4) is such that only one term in the sum contributes significantly.

This part of the proof also follows the ideas of Ruelle but it is explicitly taken into account that since f is a convex function of the number density, it is only a function that is almost everywhere differentiable. Fisher's paper is important because it clearly recognizes the problem of the thermodynamic equivalence of ensembles.

Mazur and van der Linden⁽¹⁴⁾ tried to extend Khinchin's⁽¹⁵⁾ asymptotic formula for the microcanonical partition function to systems of interacting particles. As a by-product of their proof they tried to establish the thermodynamical equivalence of the microcanonical and canonical ensembles. Starting with van Hove's, Ruelle's or Fisher's proof of the thermodynamic limit in the canonical ensemble they find the asymptotic form of the microcanonical partition function using a central limit of probability theory. For this relation it is easy to establish that $s = s(\epsilon, \rho)$ and $f = f(\beta, \rho)$ are related

by a Legendre transform wherever $f = f(\beta, \rho)$ is analytic. This proof, however, is based on the assumption that $f = f(\beta, \rho)$ is an analytic function of (real) β except at most, on a finite number of points. This assumption, although reasonable on physical grounds, cannot be rigorously established in general.

Since Ruelle's and Fisher's classical work the subject has received considerable attention. van der Linden⁽¹⁶⁾ attempted to cover a very extensive program in the foundations of thermodynamics. Under the assumptions that the potential U is made up of pair potentials, that U is stable and strongly tempered, i.e., that $A = 0$ in eqn.(1.14), van der Linden proved the existence of a thermodynamic limit for the microcanonical, canonical and grand canonical ensembles. He did not consider shape dependence on Λ , which he assumed to be a cylinder of base A and height H . The limiting process consists in letting H increase indefinitely. In this sense, it is only a one-dimensional thermodynamic limit. To prove the equivalence of ensembles, he assumes there is only one point where $f = f(\beta, \rho)$ is not differentiable in β and only one point where $p = p(\beta, \mu)$ is not differentiable in μ . It is possible that the proofs could be extended to the case where the number of points where f or p are non-differentiable is finite. However, as we mentioned before, this assumption cannot be proven rigorously. This is the only paper in which the thermodynamic limits for the three ensembles are treated independently. Following the same method, van der Linden and Mazur⁽¹⁷⁾, extended these results to other ensembles, in particular the pressure ensemble.

As remarked in section 2, generalized Legendre transforms of convex functions play a very important role in the problem of the thermodynamic equivalence of ensembles. This was not completely appreciated in the

papers we have mentioned so far. The use of generalized Legendre transforms removes the need to assume that the thermodynamic limit function we are interested in is differentiable except, at most, in a finite number of points (c.f. Appendices A and B). In a short note, Galgani, Manzoni and Scotti⁽¹⁸⁾, used generalized Legendre transforms and a simple change of variables to simplify van der Linden's proof.

Ruelle⁽¹⁹⁾, using the ideas of Fisher⁽⁹⁾ and of his 1963 paper solved the problem of the thermodynamic limit for the three ensembles and the problem of their equivalence in the most complete form known. His assumptions on the potential and the limiting process are the same as those used by Fisher⁽⁹⁾. His main result is

THM.1.1. (Ruelle) Let $S_\Lambda = S_\Lambda(E, N)$ be defined by eqn.(1.5) for a stable and tempered potential. There exist

- (a) $\rho_{cp} > 0$ or $\rho_{cp} = \infty$. ρ_{cp} is the highest possible density, the close packing density ;
- (b) a convex continuous function ϵ_0 on the interval $[0, \rho_{cp}]$ such that $\epsilon_0(0) = 0$ and $\epsilon_0(\rho) \geq -\rho B$;
- (c) a concave function s on the region $\Theta = \{(\epsilon, \rho) : 0 \leq \rho \leq \rho_{cp}, \epsilon > \epsilon_0(\rho)\}$, increasing in ϵ for fixed ρ and such that $s(0, \epsilon) = 0$ for $\epsilon > 0$.

Let $\Lambda \rightarrow \infty$ in the sense of Fisher and

$$\lim V^{-1}(\Lambda)N = \rho, \quad \lim V^{-1}(\Lambda)E = \epsilon;$$

- (α) if $(\epsilon, \rho) \in \Theta$, then

$$\lim V^{-1}(\Lambda)S_\Lambda(E, N) = s(\epsilon, \rho);$$

- (β) if (ϵ, ρ) belongs to the boundary of Θ , then

$$\overline{\lim} V^{-1}(\Lambda)S_\Lambda(E, N) \leq s(\epsilon, \rho),$$

where $s(\epsilon, \rho) = \overline{\lim} s(\epsilon, \rho)$ when $(\epsilon, \rho) \in \Theta$ and $(\epsilon, \rho) \rightarrow (\epsilon, \rho)$;

(γ) if (ϵ, ρ) belongs to the complement of the closure of Θ , then

$$\lim V^{-1}(\wedge) s_{\wedge}(E, N) = -\infty.$$

It is important to note that this theorem establishes the domain of definition of the entropy density $s = s(\epsilon, \rho)$ and its behaviour on the boundary. Once this theorem is proved, which is not an easy task, $f = f(\beta, \rho)$ is defined through eqn.(1.11) and the theorem quoted above is used to prove that eqn.(1.9) holds. In a similar manner, the equivalence with the grand canonical ensemble is proved. The idea behind the proof, is the same as that used by Fisher⁽⁹⁾. However, Ruelle does not provide these proofs in a systematic way in order that the method be extended to other ensembles. The interesting point to note is the way in which the thermodynamic limit for the canonical and grand canonical ensembles is solved simultaneously with the problem of the thermodynamic equivalence of the microcanonical, canonical and grand canonical ensembles.

One of the obvious facts that arises from analyzing the different partition functions is that they can be written as (continuous or discrete) Laplace transforms of the microcanonical partition function. For example, we see from eqn.(1.2) that $Q_{\wedge}(\beta, N)$ is the Laplace transform of $\Omega_{\wedge}(E, N)$ that replaces E by β . On the other hand, $s = s(\epsilon, \rho)$ and $f = f(\beta, \rho)$ are also related by a generalized Legendre transform that replaces ϵ by β . This pattern is general and carries on for any conceivable partition function. It would then seem reasonable to try to find a relation valid in the thermodynamic limit between Laplace transforms and generalized Legendre transforms. This is precisely what

Galgani, Scotti and Valz Gris⁽³⁾, attempted. Let $\{Q_\lambda(x)\}$ be a family of real valued functions of the real variable x parameterized by the real parameter λ . Let

$$f_\lambda(x) = \frac{1}{\lambda} \log Q_\lambda(x), \quad f(x) = \lim_{\lambda \rightarrow \infty} f_\lambda(x)$$

and

$$\psi_\lambda(t) = \frac{1}{\lambda} \log Z_\lambda(t),$$

where

$$Z_\lambda(t) = t \int_{-\infty}^{\infty} \exp(-tx) Q_\lambda(x) dx.$$

($Z_\lambda(t)$ may also be defined as the discrete Laplace transform of $Q_\lambda(x)$).

Then, under a set of general conditions satisfied by the partition functions of every ensemble if the potential U is stable, Galgani, Scotti and Valz Griss proved that

$$\lim_{\lambda \rightarrow \infty} \psi_\lambda(t) = \sup_x [f(x) - tx].$$

If the existence and convexity properties of $s = s(\epsilon, \rho)$ are established, as for example in Ruelle's book, then the result above establishes immediately the thermodynamic limit for the canonical and grand canonical ensembles and the thermodynamic equivalence of the three ensembles. This is a very elegant and simple proof of the thermodynamic equivalence of ensembles ; its only drawback is that it does not consider the boundary of the domain of definition of $s = s(\epsilon, \rho)$.

Galgani, Manzoni and Scotti⁽⁹⁾ published a unified and simple proof of the thermodynamic equivalence of ensembles, taking thm.1.1 as starting point. Their proof has the benefit that it applies to any ensemble of equilibrium classical statistical mechanics and that it considers the behaviour on the boundary of the domain of definition of thermodynamic limit functions. In the next section we present

a short discussion of their work.

Before doing so, a comment on the definition of the microcanonical partition function, eqn.(1.2). The microcanonical partition is also commonly defined replacing δ^- by δ^Δ or for δ in eqn.(1.2). The symbol δ^Δ denotes the characteristic function of the interval $(-\Delta, 0)$ where Δ is assumed to be a small positive number, and δ denotes the Dirac- δ function. We let $S_\Delta^\Delta(E, N)$ and $S'_\Delta(E, N)$ denote the resulting entropies. Galgani, Scotti and Valz Gris⁽²⁰⁾ proved that

$$\lim v^{-1}(\Delta) S_\Delta^\Delta(E, n) = \lim v^{-1}(\Delta) S'_\Delta(E, n).$$

This was also proved by van der Linden⁽¹⁶⁾ as a by-product of the proof of the thermodynamic limit of the microcanonical temperature. On the other hand, Ruelle⁽¹³⁾ proved that the above equation holds when one replaces S'_Δ by S_Δ^Δ . This, in principle solves the problem of the thermodynamical equivalence of the microcanonical ensembles.

4. A PROOF OF THE THERMODYNAMIC EQUIVALENCE OF ENSEMBLES

We present briefly the proof given by Galgani, Manzoni & Scotti⁽⁴⁾, of the thermodynamic equivalence of the equilibrium ensembles of classical statistical mechanics. The starting point of the proof is thm. 1.1 which establishes the existence of the thermodynamic limit entropy density and is based on an idea used by Ruelle⁽¹⁹⁾, in the proof of the convergence of the microcanonical entropy density given the convergence of the configurational microcanonical entropy density. As mentioned before, the importance of this work lies in the fact that the method of proof is simple and can be applied to any ensemble of equilibrium classical statistical mechanics. This paper also has the merit of dealing rigorously with the boundary of the region where the thermodynamic limit entropy density is defined.

Let f be defined by eqn. (1.11). We define the function f^* by

$$f^*(\beta) = \lim_{\substack{\rho \rightarrow \rho_{cp} \\ \rho < \rho_{cp}}} f(\beta, \rho). \quad (1.15)$$

With this notation we then have

THM 1.2 - (Galgani, Manzoni & Scotti). Let the potential U be stable and tempered and Λ growing indefinitely in the sense of Fisher. Let Q_Λ , Ξ_Λ , f , p and f^* be the functions defined by eqns. (1.3), (1.4), (1.11), (1.12) and (1.15) respectively.

(a) (i) Let $V^{-1}(\Lambda)N \rightarrow \rho$ as $\Lambda \rightarrow \infty$ with $0 \leq \rho < \rho_{cp}$. Then

$$\lim_{\Lambda \rightarrow \infty} V^{-1}(\Lambda) \log Q_\Lambda(\beta, N) = f(\beta, \rho) \quad (1.16)$$

and f is a convex function of β and a concave function of ρ .

(ii) If $\rho = \rho_{cp}$, then

$$\lim_{\Lambda \rightarrow \infty} v^{-1}(\Lambda) \log Q_{\Lambda}(\beta, N) \leq f^*(\beta).$$

(iii) If $\rho > \rho_{cp}$, then

$$\lim_{\Lambda \rightarrow \infty} v^{-1}(\Lambda) \log Q_{\Lambda}(\beta, N) = -\infty.$$

(b) $\lim_{\Lambda \rightarrow \infty} v^{-1}(\Lambda) \log \Xi_{\Lambda}(\beta, \mu) = p(\beta, \mu)$

and p is a convex function of β and ρ .

Proof :

The convexity properties of the functions f and p follow from those of the thermodynamic limit entropy density s with the help of Thm. A.5 (see Appendix A), and from the fact that if the generalized Legendre transform is performed on only one of the variables, the convexity of the other is reversed (because of the minus sign appearing in eqn. (A.2) of Appendix A, c.f. Galgani & Scotti⁽²¹⁾).

We now prove statement (a)-(i). We define

$$Q_{\Lambda}^{+}(\beta, n) = \sup_{\mathbf{E}} [\exp(-\beta E) \Omega_{\Lambda}(E, n)]. \quad (1.17)$$

Let $\{\Lambda_t\}_{1 \leq t < \infty}$ be any sequence of containers growing indefinitely in the sense of Fisher and $\{n_t\}_{1 \leq t < \infty}$ a sequence of positive integers such that $n_t v^{-1}(\Lambda_t) \rightarrow \rho$ as $t \rightarrow \infty$. Given $\delta > 0$ sufficiently

small and Λ_{t0} sufficiently large, we see from eqns (1.11), (1.5) and (1.8), that we can choose n_t and E_t in such a way that

$$\exp(-\beta E_t) \Omega_{\Lambda_t}(E_t, n_t) \geq \exp[V(\Lambda_t)(f(\beta, \rho) - \delta)]. \quad (1.18)$$

On the other hand, for sufficiently large Λ and all n and E

$$\exp(-\beta E) \Omega_{\Lambda}(E, n) \leq \exp[V(\Lambda)(f(\beta, \rho) + \delta)]. \quad (1.19)$$

Then, from eqns. (1.17)-(1.19)

$$\lim V^{-1}(\Lambda) \log Q_{\Lambda}^{+}(\beta, n) = f(\beta, \rho). \quad (1.20)$$

On the other hand let $E' \geq -nB$. Then

$$Q_{\Lambda}(\beta, n) \geq \beta \int_{E'}^{\infty} dE \exp(-\beta E) \Omega_{\Lambda}(E, n) \geq \exp(-\beta E') \Omega_{\Lambda}(E', n),$$

where an integration by parts has been carried out. Then

$$\exp(-\beta E) \Omega_{\Lambda}(E, n) \leq Q_{\Lambda}^{+}(\beta, n) \leq Q_{\Lambda}(\beta, n). \quad (1.21)$$

Let $\beta' < \beta$. Then, using the first inequality in (1.21)

$$Q_{\Lambda}(\beta, n) \leq \frac{\beta}{\beta - \beta'} Q_{\Lambda}^{+}(\beta', n) \exp(\beta - \beta')nB. \quad (1.22)$$

From eqns. (1.21) and (1.22) it follows that

$$\begin{aligned} V^{-1}(\Lambda) \log Q_{\Lambda}^{+}(\beta, n) &\leq V^{-1}(\Lambda) \log Q_{\Lambda}(\beta, n) \leq V^{-1}(\Lambda) \log Q_{\Lambda}^{+}(\beta', n, \Lambda) \\ &\quad + V^{-1}(\Lambda) \log \left(\frac{\beta}{\beta - \beta'} \right) + V^{-1}(\Lambda) (\beta - \beta')nB. \end{aligned}$$

This concludes the proof of the theorem, since the thermodynamic limit exists for $Q_{\Lambda}^{+}(\beta, n)$ and f is a continuous function of β .

The same method of proof can be used for the rest of the theorem and also for any ensemble of equilibrium classical statistical mechanics.

5. CONCLUSIONS

We have shown how the problem of the thermodynamic equivalence of ensembles has evolved and its close relationship with the problem of the thermodynamic limit for the different ensembles. In particular, we have shown that the most satisfactory way in which both problems can be solved is by first solving the problem of the thermodynamic limit for the microcanonical ensemble, then to define the functions f and p by

$$f(\beta, \rho) = \sup_{\epsilon} [s(\epsilon, \rho) - \beta \epsilon] \quad (1.23)$$

and

$$p(\beta, \mu) = \sup_{\rho} [f(\beta, \rho) - \mu \rho] \quad (1.24)$$

where s is the thermodynamic limit entropy density, and finally use Thm. 1.2 to show that

$$\lim_{\Lambda \rightarrow \infty} V^{-1}(\Lambda) \log Q_{\Lambda}(\beta, N) = f(\beta, \rho)$$

and

$$\lim_{\Lambda \rightarrow \infty} V^{-1}(\Lambda) \log \Xi_{\Lambda}(\beta, \mu) = p(\beta, \mu)$$

where Q_{Λ} and Ξ_{Λ} are defined by eqns. (1.3) and (1.4) respectively.

Thm. 1.2 also establishes the convexity properties of f and p , and the behavior of f on the boundary of its domain of definition. This theorem can be extended straight forwardly to any equilibrium ensemble of classical statistical mechanics.

The only question that remains to be answered is whether the fact that the functions s , f and p are related by the appropriate generalized Legendre transforms in fact guarantees that the thermodynamic descriptions obtained through these functions are equivalent. We look into this question for the case of the functions s and f , although the same comments apply in general.

The first order partial derivatives of the functions s or f define the intensive parameters (temperature, pressure, etc.) while the second order partial derivatives define the calorific parameters (specific heats, compressibility, etc.). We know that the thermodynamic limit inverse temperature β is defined by

$$\beta(\epsilon, \rho) = \frac{\partial s(\epsilon, \rho)}{\partial \epsilon} \quad (1.25)$$

and the specific heat c by

$$c(\epsilon, \rho) = \left[- \frac{\partial^2 s(\epsilon, \rho)}{\partial \epsilon^2} \right]^{-1}. \quad (1.26)$$

Since s is concave in ϵ , the thermodynamic limit inverse temperature β is a decreasing function, continuous except, at most, on a countable number of points for fixed ρ ⁵.

5 In fact, as we will prove in the next chapter, β is a continuous function of ϵ . However, since we are taking the partial order derivatives of s as an example of a relation that must hold true for any pair of ensembles, we do not assume the continuity of β .

The second order partial derivative of the thermodynamic entropy density with respect to the energy density is continuous except, at most, on a countable number of points for fixed ρ , since it is the derivative of a non-increasing function⁽²²⁾.

On the other hand, starting from the function f , we know that the energy density ϵ is defined by

$$\epsilon(\beta, \rho) = - \frac{\partial f(\beta, \rho)}{\partial \beta} \quad (1.24)$$

and the specific heat c (which is now a function of β and ρ) is defined by

$$c(\beta, \rho) = - \frac{\partial^2 f(\beta, \rho)}{\partial \beta^2} . \quad (1.25)$$

The fact that f is the (minus) generalized transform of s guarantees that the function $\beta(\epsilon, \rho)$ is the inverse of the function $\epsilon(\beta, \rho)$ for fixed ρ (see Appendix A, Thm. A.5). Wherever β is differentiable in ϵ and its derivative with respect to ϵ is less than zero, we can use the inverse function theorem⁽²³⁾ and conclude that

$$c(\beta, \rho) = c(\epsilon, \rho).$$

Hence, the thermodynamic description obtained through the function s is equivalent to that obtained through the function f , whenever the thermodynamic parameters are defined.

CHAPTER 2. CONTINUITY OF THE TEMPERATURE AND DERIVATION OF THE GIBBS CANONICAL DISTRIBUTION IN CLASSICAL STATISTICAL MECHANICS.

1. INTRODUCTION

For any system in statistical mechanics, experience leads us to believe that the temperature is a continuous function of the energy. That is, we expect that no matter how simple or complicated a system may be, its thermodynamical behavior will be such that no 'phase transition' will occur in which the temperature changes abruptly. In this paper we give a rigorous proof that for a classical system of particles the thermodynamic limit entropy density is a differentiable function of the energy density and that its derivative, the thermodynamic limit inverse temperature, is a continuous function of the energy density. We also prove that the inverse temperature of a finite system approaches the thermodynamic limit inverse temperature as the volume of the finite system increases indefinitely. As a corollary, we show that the probability distribution of a small system in thermal contact with a large one approaches the Gibbs canonical distribution as the large system increases indefinitely, if the composite system is distributed microcanonically.

The proofs follow from the properties of convex functions. In particular, the continuity of the thermodynamic limit inverse temperature as a function of the energy density follows from the concavity of the thermodynamic limit entropy density and the convexity in the energy density of a certain monotonic function of the thermodynamic limit entropy density. The convexity of this

function is established with the help of the Schwarz inequality. The only assumptions needed for these results are the stability and temperedness of the potential ⁽²⁹⁾.

2. DEFINITIONS

We consider a system of n identical particles of mass m enclosed in a v -dimensional container Λ with total energy E .

The microcanonical partition function Ω_Λ is defined by

$$\Omega_\Lambda(E, n) = (n!)^{-1} \int_{\Lambda^n} d\mathbf{x} \int_{\mathbb{R}^{nv}} d\mathbf{p} \delta^-[E - H(\mathbf{x}, \mathbf{p})], \quad (2.1)$$

where $(\mathbf{x}, \mathbf{p}) = (x_1, \dots, x_n, p_1, \dots, p_n)$, $d\mathbf{x} = dx_1 \dots dx_n$, $d\mathbf{p} = dp_1 \dots dp_n$ with $x_i \in \Lambda$, $p_i \in \mathbb{R}^v$. The symbols x_i and p_i respectively denote the position and momentum vectors of the i th particle. The symbol δ^- denotes the unit step function, and H is the Hamiltonian of the system defined by

$$H(\mathbf{x}, \mathbf{p}) = (2m)^{-1} \sum_{i=1}^n p_i^2 + U(\mathbf{x}),$$

where U denotes the potential energy.

Let $E_\Lambda^{(0)}$ denote the infimum of the potential U for $\mathbf{x} \in \Lambda^n$, which exists since the potential U is stable. Then, if $E > E_\Lambda^{(0)}$, we define the entropy S_Λ , taking units where Boltzmann's constant is 1, by

$$S_\Lambda(E, n) = \log \Omega_\Lambda(E, n). \quad (2.2)$$

The entropy density s_Λ , which is a function of the energy density ϵ and the number density ρ , is defined by

$$s_\Lambda(\epsilon, \rho) = v^{-1}(\Lambda) S_\Lambda(E, n), \quad (2.3)$$

where $\varepsilon = E/V(\Lambda)$ and $\rho = n/V(\Lambda)$ and $V(\Lambda)$ denotes the volume of the container Λ .

For $\varepsilon > \varepsilon_{\Lambda}^{(0)}$, where $\varepsilon_{\Lambda}^{(0)} = E_{\Lambda}^{(0)}/V(\Lambda)$, the inverse temperature β_{Λ} is defined by

$$\beta_{\Lambda}(\varepsilon, \rho) = \frac{\partial s_{\Lambda}(\varepsilon, \rho)}{\partial \varepsilon} = \frac{\Omega'_{\Lambda}(E, n)}{\Omega_{\Lambda}(E, n)}, \quad (2.4)$$

where Ω'_{Λ} denotes the partial derivative of Ω_{Λ} with respect to E .

The thermodynamic limit entropy density is defined⁽³⁰⁾ by

$$s(\varepsilon, \rho) = \lim_{\Lambda \rightarrow \infty} s_{\Lambda}(\varepsilon_{\Lambda}, \rho_{\Lambda}), \quad (2.5)$$

where $\{\varepsilon_{\Lambda}\}$ and $\{\rho_{\Lambda}\}$ are sequences which approach ε and ρ as Λ increases indefinitely in the sense of Fisher. The function s is defined on a certain convex set Θ (whose exact definition is not important for our purposes).

The thermodynamic limit entropy density is a concave function of ε ⁽³⁰⁾. Hence⁽³¹⁾, the left and right hand partial derivatives with respect to ε exist for all $(\varepsilon, \rho) \in \Theta$. Denoting these derivatives by β_{-} and β_{+} respectively, they must satisfy the inequality

$$\beta_{+}(\varepsilon, \rho) \leq \beta_{-}(\varepsilon, \rho). \quad (2.6)$$

Wherever the left and right derivatives of s with respect to ε coincide they are continuous⁽³²⁾ and we define the thermodynamic limit inverse temperature β as this common value.

3. CONTINUITY OF THE TEMPERATURE

We start by proving that in the microcanonical ensemble formalism the thermodynamic limit entropy density s is a differentiable function of the energy density and that the thermodynamic limit inverse temperature β is continuous in the energy density ϵ . The proof follows from the concavity of s and the convexity in ϵ of a function σ related to s by Eq. (2.10) below. Next, we prove that the inverse temperature of a finite system approaches the thermodynamic limit inverse temperature as the volume of the finite system increases indefinitely.

If we integrate Eq.(2.1) with respect to the momenta, we find that

$$\Omega_{\Lambda}(E, n) = \frac{(2\pi m)^{nv/2}}{n! \Gamma(\frac{nv}{2} + 1)} \int_{\Lambda^n} d\mathbf{x} [E - U(\mathbf{x})]^{nv/2} \delta^{-}[E - U(\mathbf{x})], \quad (2.7)$$

where Γ denotes the gamma function.

From Eq. (2.4) we note that

$$\frac{\partial \beta_{\Lambda}(\epsilon, \rho)}{\partial \epsilon} = v(\Lambda) \beta_{\Lambda}^2(\epsilon, \rho) \left[\frac{\Omega_{\Lambda}(E, n) \Omega_{\Lambda}''(E, n)}{(\Omega_{\Lambda}'(E, n))^2} - 1 \right], \quad (2.8)$$

where Ω_{Λ}'' denotes the partial derivative of Ω_{Λ}' with respect to E . By differentiating formula (7) we can obtain integral formulae for $\Omega_{\Lambda}'(E, n)$ and $\Omega_{\Lambda}''(E, n)$. These integrals are related,

if $n\nu/2 \geq 2$, by Schwarz inequality

$$\left\{ \int_{\Lambda^n} d\mathbf{x} [E-U(\mathbf{x})]^{n\nu/2-1} \delta^-[E-U(\mathbf{x})] \right\}^2 \\ \leq \int_{\Lambda^n} d\mathbf{x} [E-U(\mathbf{x})]^{n\nu/2} \delta^-[E-U(\mathbf{x})] \int_{\Lambda^n} d\mathbf{x} [E-U(\mathbf{x})]^{n\nu/2-2} \delta^-[E-U(\mathbf{x})].$$

From this inequality and Eq. (2.7) we obtain

$$\frac{\Omega_{\Lambda}(E,n)\Omega_{\Lambda}''(E,n)}{(\Omega_{\Lambda}'(E,n))^2} \geq 1 - \frac{2}{n\nu}.$$

Using this in Eq. (2.8) we find that

$$\frac{\partial \beta_{\Lambda}(\epsilon, \rho)}{\partial \epsilon} + \frac{2}{\nu \rho} \beta_{\Lambda}^2(\epsilon, \rho) \geq 0. \quad (2.9)$$

Now, let σ_{Λ} be the function defined by

$$\sigma_{\Lambda}(\epsilon, \rho) = \exp\left(\frac{2}{\nu \rho} s_{\Lambda}(\epsilon, \rho)\right). \quad (2.10)$$

Then

$$\frac{\partial^2 \sigma_{\Lambda}(\epsilon, \rho)}{\partial \epsilon^2} = \frac{2}{\nu \rho} \sigma_{\Lambda}(\epsilon, \rho) \left[\frac{\partial \beta_{\Lambda}}{\partial \epsilon}(\epsilon, \rho) + \frac{2}{\nu \rho} \beta_{\Lambda}^2(\epsilon, \rho) \right].$$

From this expression and inequality (2.9) it follows that σ_{Λ}

is convex in ϵ . Let σ be the thermodynamic limit of σ_Λ , which exists in view of Eq. (2.5). That is,

$$\sigma(\epsilon, \rho) = \lim_{\Lambda \rightarrow \infty} \sigma_\Lambda(\epsilon, \rho) = \exp\left(\frac{2}{\nu\rho} s(\epsilon, \rho)\right). \quad (2.11)$$

The function σ is convex in ϵ since it is the limit of a sequence of convex functions⁽³³⁾. Hence, its left and right hand derivatives with respect to ϵ , which we denote by $\partial\sigma/\partial\epsilon_-$ and $\partial\sigma/\partial\epsilon_+$ respectively, exist, are continuous except, at most, on a countable number of points, and satisfy the inequality

$$\frac{\partial\sigma(\epsilon, \rho)}{\partial\epsilon_-} \leq \frac{\partial\sigma(\epsilon, \rho)}{\partial\epsilon_+}.$$

By Eq. (2.11) this implies that

$$\beta_-(\epsilon, \rho) \leq \beta_+(\epsilon, \rho). \quad (2.12)$$

From inequalities (2.6) and (2.12) it follows that $\beta_- = \beta_+$ for all ϵ and hence that the thermodynamic limit entropy density s is a differentiable function of ϵ and that its derivative, the thermodynamic limit inverse temperature β is continuous in ϵ .

There is a theorem on convex functions^(34,35) which states that if a sequence of differentiable convex functions has a limit then the sequence of derivatives converges to the derivative of the limit function at the points where the latter is continuous. Applying this theorem to the sequence of functions σ_Λ , we have

$$\lim_{\Lambda \rightarrow \infty} \frac{\partial \sigma_{\Lambda}(\epsilon, \rho)}{\partial \epsilon} = \frac{\partial \sigma(\epsilon, \rho)}{\partial \epsilon},$$

since $\partial \sigma(\epsilon, \rho) / \partial \epsilon$ is continuous in ϵ . This result may also be written

$$\lim_{\Lambda \rightarrow \infty} \beta_{\Lambda}(\epsilon, \rho) = \beta(\epsilon, \rho). \quad (2.13)$$

4. DERIVATION OF THE CANONICAL DISTRIBUTION⁸

To prove that a finite system in thermal contact with an infinite heat bath is distributed canonically, we first use the above results to show that in the thermodynamic limit

$$\lim_{\Lambda \rightarrow \infty} \frac{\Omega_{\Lambda}(E - \Delta E, n)}{\Omega_{\Lambda}(E, n)} = \exp[-\Delta E \beta(\epsilon, \rho)], \quad (2.14)$$

whenever $E/V(\Lambda) \rightarrow \epsilon$, $n/V(\Lambda) \rightarrow \rho$ with $(\epsilon, \rho) \in \Theta$ as Λ increases indefinitely in the sense of Fisher, and $\Delta E \geq 0$ is arbitrary and does not depend on Λ .

Fix $(\epsilon, \rho) \in \Theta$ and choose $\Delta \epsilon \neq 0$ in such a way that $(\epsilon - \Delta \epsilon, \rho) \in \Theta$. Since σ_{Λ} is a differentiable function of ϵ , we may define the function Φ_{Λ} by

$$\sigma_{\Lambda}(\epsilon - \Delta \epsilon, \rho) - \sigma_{\Lambda}(\epsilon, \rho) = \frac{-\Delta \epsilon}{V\rho} \sigma_{\Lambda}(\epsilon, \rho) \cdot \beta_{\Lambda}(\epsilon, \rho) - \Phi_{\Lambda}(\epsilon, \rho, \Delta \epsilon)$$

where

$$\lim_{\Delta \epsilon \rightarrow 0} \frac{\Phi_{\Lambda}(\epsilon, \rho, \Delta \epsilon)}{\Delta \epsilon} = 0.$$

This expression can be written more conveniently as

$$\frac{\sigma_{\Lambda}(\epsilon - \Delta \epsilon, \rho)}{\sigma_{\Lambda}(\epsilon, \rho)} = 1 - \frac{\Delta \epsilon}{V\rho} \beta_{\Lambda}(\epsilon, \rho) - \varphi_{\Lambda}(\epsilon, \rho, \Delta \epsilon), \quad (2.15)$$

where $\varphi_{\Lambda} = \Phi_{\Lambda}/\sigma_{\Lambda}$ and

8. The proof of Eq. (2.14) below is different of the one that appears in the paper submitted for publication.

$$\lim_{\Delta \epsilon \rightarrow 0} \frac{\varphi_{\Lambda}(\epsilon, \rho, \Delta \epsilon)}{\Delta \epsilon} = 0. \quad (2.16)$$

In view of Eq. (2.11) and (2.13) φ_{Λ} converges as Λ increases indefinitely at fixed $\Delta \epsilon$. On the other hand, by differentiating Eq. (2.15) twice with respect to $\Delta \epsilon$ and taking into account inequality (2.9), we find that φ_{Λ} is convex in $\Delta \epsilon$. Hence, as a function of $\Delta \epsilon$, the convergence of φ_{Λ} is uniform in a sufficiently small neighbourhood of the origin, since convergence of a sequence of convex functions implies uniform convergence in any closed interval contained in the domain of the limit function⁽³³⁾.

Now, let $\Delta \epsilon = \Delta E/V(\Lambda)$ where $\Delta E \neq 0$ does not depend on Λ , so that $\Delta \epsilon \rightarrow 0$ as Λ grows indefinitely. Using equations (2.2), (2.3), (2.10) and (2.15) we may write

$$\begin{aligned} \frac{\Omega_{\Lambda}(E - \Delta E, n)}{\Omega_{\Lambda}(E, n)} &= \left[\frac{\sigma_{\Lambda}(\epsilon - \Delta \epsilon, \rho)}{\sigma_{\Lambda}(\epsilon, \rho)} \right]^{n\nu/2} \\ &= 1 - \frac{2}{n\nu} \left[\Delta E \cdot \beta_{\Lambda}(\epsilon, \rho) + \frac{\nu \rho \Delta E}{2} \left(\frac{\varphi_{\Lambda}(\epsilon, \rho, \Delta \epsilon)}{\Delta \epsilon} \right) \right]^{n\nu/2}, \end{aligned}$$

where we have used the relation $\Delta \epsilon = \Delta E \rho / n$. From this expression, the uniform convergence of φ_{Λ} and Eq. (2.16), Eq. (2.14) follows.

We now consider a finite system $S^{(1)}$, whose Hamiltonian we denote by $H^{(1)}$, in thermal contact with a system $S^{(2)}$

enclosed in a finite container Λ , which we call the heat bath.

We want to find the probability distribution for $S^{(1)}$,

when the composite system is distributed microcanonically and $S^{(2)}$ grows indefinitely while $S^{(1)}$ remains unchanged. We know⁽³⁶⁾ that the probability measure $\mu_{\Lambda}^{(1)}$ on the phase space of $S^{(1)}$ is given by

$$\mu_{\Lambda}^{(1)}(\underline{x}, \underline{p}) = c_{\Lambda} \Omega_{\Lambda}(E_{\Lambda} - H^{(1)}(\underline{x}, \underline{p}), n), \quad (2.17)$$

where now $(\underline{x}, \underline{p})$ denotes a point in the phase space of $S^{(1)}$, c_{Λ} is a normalizing constant given by

$$c_{\Lambda} = \left[\int d\underline{x} \int d\underline{p} \Omega_{\Lambda}(E_{\Lambda} - H^{(1)}(\underline{x}, \underline{p}), n) \right]^{-1}, \quad (2.18)$$

and the integration is carried out over the phase space of $S^{(1)}$.

Putting $\Delta E = H^{(1)}(\underline{x}, \underline{p})$ in Eq. (2.14) we then find that

$$\lim_{\Lambda \rightarrow \infty} \mu_{\Lambda}^{(1)}(\underline{x}, \underline{p}) = \frac{\exp[-\beta(\epsilon, \rho) H^{(1)}(\underline{x}, \underline{p})]}{\int d\underline{x} \int d\underline{p} \exp[-\beta(\epsilon, \rho) H^{(1)}(\underline{x}, \underline{p})]}. \quad (2.19)$$

This shows that the probability distribution for a small system in thermal contact with an infinitely large heat bath is the Gibbs canonical distribution.

5. CONCLUSIONS

We have proved that in the microcanonical ensemble formalism of classical statistical mechanics the thermodynamic limit entropy density is a differentiable function of the energy density and that its derivative, the thermodynamic limit inverse temperature, is continuous in the energy density. We have also proved that the inverse temperature of a finite system approaches the thermodynamic limit inverse temperature as the volume of the system increases indefinitely. Finally, we proved that the probability distribution for a finite classical system in thermal contact with an infinite heat bath, the composite system being distributed microcanonically, is the Gibbs canonical distribution.

There has been some previous work on these problems. Khinchin⁽³⁷⁾ derived the canonical distribution for a finite classical system of non-interacting particles in contact with an infinite heat bath using a central limit theorem of probability theory. Mazur and van der Linden⁽³⁸⁾ tried to extend Khinchin's proof to systems of interacting particles. Their proof is based on an assumption about the distribution of zeros of the canonical partition function of finite systems that implies that the thermodynamic limit free energy density is such that phase transitions may occur at most for a finite number of temperatures. In another paper, van der Linden⁽³⁹⁾ tried to prove Eq. (2.13) under the same assumptions concerning the behaviour of the thermodynamic limit free energy density.

One of the aims of equilibrium statistical mechanics is to establish sufficient conditions on the microscopic interactions in a system composed of a great number of particles, in order that

the system exhibit thermodynamic behaviour. That is, we would like to be able to prove, for suitable systems, that the postulates of thermodynamics apply in the thermodynamic limit. In Callen's⁽⁴⁰⁾ postulational approach to thermodynamics, one of the postulates is that the entropy density is a continuous and differentiable function of the energy density. Our result shows that Callen's postulate applies to classical systems of particles with stable and tempered potential.

There appears to be no difficulty in generalizing these results to other types of classical systems with kinetic degrees of freedom, but it still remains to be seen if the results hold in the quantum mechanical case.

CHAPTER 3 CORRELATION INEQUALITIES FOR FERROMAGNETIC ISING SPIN SYSTEMS AND THE DUPLICATE VARIABLE METHOD

1. INTRODUCTION

Correlation inequalities play an important role in the rigorous investigations concerning the ferromagnetic Ising spin system. They are used, for example, to prove the existence of the thermodynamic limit for the correlation functions ^(41,42,43), to obtain a lower bound on the magnetization of the Ising model on a square lattice ⁽⁴⁴⁾, to obtain upper and lower bounds on critical temperatures ^(45,46), and to prove the existence of a sharp interface at low temperatures for nearest neighbour interactions on a three dimensional lattice ⁽⁴⁷⁾. Correlation inequalities (in particular the GHS inequality) have also been used to prove the concavity of the magnetization ⁽⁴⁸⁾, to establish the absence of certain bound states in quantum field theory ^(49,50), to derive critical point exponents ⁽⁴⁸⁾ and to prove eigenvalue inequalities in quantum mechanics ⁽⁵¹⁾.

The methods by which these inequalities were first obtained are various, sometimes quite complicated. In this chapter, we describe a simple method for deriving correlation inequalities. We refer to it as the duplicate variable method. This method is not a rigidly defined recipe, but a technique that with many variants has been applied successfully to give simple and unified proofs of correlation inequalities.

If, for example, we want to prove that a certain product of n correlation functions is non-negative, the method consists in expressing

this product as an expectation of a suitable function over a larger space obtained by considering n or more copies of the original system. The next step is to introduce new variables through a transformation that is usually orthogonal in such a way that it appears clearly that we are calculating the expectation of a non-negative function.

The method was fully employed for the first time by Percus ⁽⁵²⁾, although elements of it appeared in work done previously. In the next section we introduce the necessary notation and definitions and discuss the more general inequalities. In Section 3 we discuss the duplicate variable method and give examples of how the method is used. In particular, we present van Beijeren's proof ⁽⁴⁷⁾ of the existence of a sharp interface at sufficiently low temperature for an Ising ferromagnet with nearest-neighbour interactions in three or more dimensions.

2. CORRELATION INEQUALITIES FOR FERROMAGNETIC ISING SPIN SYSTEMS

The Ising spin system has received very much attention due to the fact that it is probably the simplest many-body system that can be studied rigorously, (for a historical review see Brush,⁽⁵³⁾ for a review of more recent results see Ruelle⁽¹³⁾, Griffiths^(7,54) and Lebowitz⁽⁵⁵⁾). In these studies correlation inequalities play an important role since, for example, the state of the system may be defined by the set of correlations. In this section we present some of the correlation inequalities most often used in the investigations of the Ising spin system and describe briefly how they were first obtained. In the next section we will again look at the subject using the duplicate variable method.

For our purposes it is convenient to define the Ising spin ferromagnet system in a very general context. A generalised Ising ferromagnet is a triple (Λ, H, ν) where:

(i) Λ is a finite set which is referred to as a finite lattice. The elements of Λ are known as sites. Since Λ is finite, we usually number the elements of Λ and write $\Lambda = \{1, \dots, N\}$ where N is the cardinality of Λ . With each site $i \in \Lambda$ we associate a real spin variable $\sigma_i \in \mathbb{R}$. The product space $X = \prod_{i \in \Lambda} \mathbb{R}$ is known as the configuration space and a configuration of Λ is an N -dimensional vector $\underline{\sigma} = (\sigma_1, \dots, \sigma_N)$. The sites of Λ are interpreted as the positions of atoms in a crystal and the spin variable σ_i at each site $i \in \Lambda$ as a classical version of the quantum mechanical spin associated with the atom at the site i . A point $\underline{\sigma} \in X$ corresponds to a state of the system.

(ii) The Hamiltonian H is a real valued function on the configuration space defined by

$$H(\sigma) = - \sum_{A \subset \Lambda} J_A \sigma_A, \quad (3.1)$$

where

$$\sigma_A = \prod_{i \in A} \sigma_i.$$

The symbols J_A denote the interaction constants and the ferromagnetic assumption is that $J_A \geq 0$ for $A \subset \Lambda$ if A contains more than one site^(*). The Hamiltonian H is a polynomial in the variables σ_i . The linear term $-\sum_{i \in \Lambda} J_i \sigma_i$ is commonly thought of as describing the effect of an external magnetic field, while higher order terms are considered to arise from mutual interactions of the spins. We recognize this by writing $-\sum_{i \in \Lambda} h_i \sigma_i$ in the Hamiltonian instead of $-\sum_{i \in \Lambda} J_i \sigma_i$. The Hamiltonian function $H(\sigma)$ is to be interpreted as the energy of the configuration σ .

(iii) The symbol ν denotes the single-spin measure and is an even Borel probability measure on \mathbb{R} . If the generalized Ising spin ferromagnet system is a model of an $\ell/2$ -spin ferromagnet, the measure ν is taken to be

$$d\nu(\sigma) = \frac{1}{\ell + 1} \sum_{j=0}^{\ell} \delta(-\ell + 2j + \sigma) d\sigma, \quad (3.2)$$

(*) We define $J_\emptyset = 0$ and $\sigma_\emptyset = 1$.

where δ denotes Dirac's δ -function. If the measure ν is continuous we require that it decay sufficiently fast for $\sigma \rightarrow \pm \infty$. More precisely, we require that

$$\int_{\mathbb{R}} \exp[a|\sigma|^d] d\nu(\sigma) < \infty \quad \forall a \in \mathbb{R},$$

where d is the degree of the polynomial H . The single-spin measure is a temperature-independent weight determined by the internal properties of the atoms. Continuous measures are of interest in the lattice approximation of quantum field theory^(56,57,58).

The Gibbs measure of (Λ, H, ν) is the probability measure μ on X defined by

$$\mu(E) = Z^{-1} \int_E \exp[-\beta H(\underline{g})] d\nu(\underline{g}), \quad (3.3)$$

where $d\nu(\underline{g}) = \prod_{i=1}^N d\nu(\sigma_i)$, E is any measurable set of X , β is the inverse temperature and Z is the partition function defined by

$$Z = \int \exp[-\beta H(\sigma)] d\nu(\sigma). \quad (3.4)$$

If f is a function defined over the configuration space X , its thermal average with respect to the Gibbs measure, which we denote by $\langle f \rangle$, is given by

$$\langle f \rangle = Z^{-1} \int f(\sigma) \exp[-\beta H(\sigma)] d\nu(\sigma). \quad (3.5)$$

A correlation function for the set of sites inside $A \subset \Lambda$ is given by $\langle \sigma_A \rangle$.

By defining the Ising spin ferromagnet in such a general context it is possible to follow the development of the correlation inequalities. In what follows we will be interested in inequalities relating different correlation functions. In order to simplify the notation we incorporate the inverse temperature in the symbols J_A . That is, for now on, the symbol J_A is to be understood as the interaction constant multiplied by β .

For an Ising spin ferromagnet one finds that for any two sites $i, j \in \Lambda$

$$\langle \sigma_i \sigma_j \rangle \geq 0, \quad (3.6)$$

and that

$$\frac{\partial \langle \sigma_k \sigma_\ell \rangle}{\partial J_{ij}} = \langle \sigma_i \sigma_j \sigma_k \sigma_\ell \rangle - \langle \sigma_k \sigma_\ell \rangle \langle \sigma_i \sigma_j \rangle \geq 0 \quad (3.7)$$

for any sites $i, j, k, \ell \in \Lambda$ ⁽⁴¹⁾. The first inequality arises from the fact that spins tend to align each other in a ferromagnet since this decreases the total energy. Since increasing the coupling constants corresponds to decreasing the temperature, inequality (3.7) expresses the fact that the correlation $\langle \sigma_k \sigma_\ell \rangle$ increases when the temperature decreases.

The inequalities (3.6) and (3.7) were first proved by Griffiths⁽⁴¹⁾ for the Hamiltonian given by eqn.(3.1) when $J_A = 0$ if A contains one

element or more than two (pair interactions in the absence of an external field), and single-spin measure given by (3.2) when $\ell = 1$. The proof was later extended⁽⁴²⁾ to include the action of an external magnetic field, that is, to the Hamiltonian

$$H(\sigma) = -\frac{1}{2} \sum_{\substack{i \neq j \\ i, j \in \Lambda}} J_{ij} \sigma_i \sigma_j - \sum_{i \in \Lambda} h_i \sigma_i, \quad (3.8)$$

where $J_{ij} = J_{ji} \geq 0$ and $h_i \geq 0$. The proof is based on the use of restricted partition functions (where the integration in eq.(3.4) is restricted to configurations where some spins have specified values), and follows by induction on the number of sites in Λ .

Following the same method of proof, Griffiths⁽⁴⁵⁾ established the inequality

$$\langle \sigma_i \sigma_j \rangle \leq \sum_{k(\neq i)} \langle \sigma_k \sigma_j \rangle \tanh J_{ik} \quad (3.9)$$

for a $\frac{1}{2}$ -spin system whose Hamiltonian includes only pair interactions, (no external field). This inequality was used by Griffiths to prove that such a ferromagnet cannot exhibit spontaneous magnetization at temperatures above the mean-field approximation to the Curie or "critical" point.

These results were extended by Kelly and Sherman⁽⁵⁹⁾ to include a general Hamiltonian of the form (3.1) with $J_A \geq 0$ for all $A \subset \Lambda$ but restricted to single-spin measure given by (3.2) with $\ell = 1$. They proved that

$$\langle \sigma_B \rangle \geq 0, \quad (3.10)$$

$$\frac{\partial \langle \sigma_B \rangle}{\partial J_C} = \langle \sigma_B \sigma_C \rangle - \langle \sigma_B \rangle \langle \sigma_C \rangle \geq 0. \quad (3.11)$$

and that if D is a subset of Λ that contains the site i , then

$$\langle \sigma_D \rangle \leq \sum_{\substack{A \in \Lambda \\ i \in A}} \tanh J_A \langle \sigma_D \sigma_A \rangle. \quad (3.12)$$

Inequalities (3.10) - (3.12) are usually referred to as the first, second and third GKS inequalities. The proof given by Kelly and Sherman follows the ideas used by Griffiths. Ruelle⁽⁶⁰⁾ presented a proof of the first and second GKS inequalities which in part follows the work of Kelly and Sherman.

Sherman⁽⁶¹⁾ and Ginibre⁽⁶²⁾, showed that eqn.(3.11) is a special case of a more general class of inequalities. However, it seems that the more general inequalities have not been useful in the problem of phase transitions.

In the paper just mentioned, Ginibre also gave a simple proof of the second GKS inequality. In this proof he uses a copy of the system to express a product of two correlation functions as a correlation of some function in a larger configuration space. This is one of the characteristics of the duplicate variable method. He also uses a simple change of variables although it is not of the form used in the duplicate variable method. His proof is reproduced in Griffiths review article⁽⁷⁾.

Griffiths⁽⁶³⁾, extended the second GKS inequality to cover the cases where the single-spin measure ν is given by eqn. (3.2) for arbitrary ℓ , and by a limiting process to the case where ν is constant in the interval $[-1,1]$. The proof also shows some of the elements we will later find in the duplicate variable method, mainly to enlarge the system over which expectations are calculated.

The main idea of the proof is to represent an Ising particle of spin $\ell/2$ in terms of a cluster of ℓ spin- $\frac{1}{2}$ particles interacting among themselves through suitable ferromagnetic interactions. Then, the original system is represented by a larger but simpler system. Each spin variable of the original system takes on the values $\ell, \ell-2, \ell-4, \dots, 2-\ell, -\ell$ and hence, may be written as

$$\sigma_i = \sum_{k=1}^{\ell} \tau_{ik}, \quad \forall i \in \Lambda, \quad (3.14)$$

where τ_{ik} are spin- $\frac{1}{2}$ variables, that is, they take on the values ± 1 . Provided the weight function $W_i(\tau_{i1}, \dots, \tau_{i\ell})$ is properly chosen we may write for arbitrary f

$$\sum_{\sigma_i} f(\sigma_i) = \sum_{\tau_{i1}} \dots \sum_{\tau_{i\ell}} W_i f(\tau_{i1} + \dots + \tau_{i\ell})$$

where the summations over the spin variables are effected over all their possible values. We say that W_1 is a ferromagnetic pair weight if it can be written in the form

$$W_i(\tau_{i1}, \dots, \tau_{i\ell}) = \exp\left[\sum_{m < n} K_{mn}(\tau_{mn} - 1)\right],$$

where $0 \leq K_{mn} \leq \infty$. By means of (3.14) the Hamiltonian of the system given by eqn.(3.1) may be expressed as a function of the new variables τ_{ij} and we define the analog Hamiltonian \hat{H} by

$$\hat{H}(\tau_{11}, \dots, \tau_{N\ell}) = H(\varrho(\tau_{11}, \dots, \tau_{N\ell})) - \sum_{j=1}^N \log W_i,$$

where $\varrho(\tau_{11}, \dots, \tau_{N\ell})$ denotes the transformations defined by (3.14).

The proof now proceeds by showing that averages using the analog Hamiltonian are equal to those employing the original Hamiltonian and that the analog Hamiltonian does indeed satisfy the assumptions required by Kelly and Sherman⁽⁵⁹⁾.

The GKS inequalities appeared in a more general context in the work of Ginibre⁽⁶⁴⁾ and Fortuin, Kasteleyn and Ginibre⁽⁶⁵⁾. In these papers again we find the use of a larger space to represent products of expectations, although no attempt is made to introduce a change of variables, which is the second characteristic of the duplicate variable method. The main result of Fortuin, Kasteleyn and Ginibre is the following: let X be a finite set and $\mathcal{P}(X)$ the set of all subsets of X . If μ is a positive measure satisfying the condition

$$\mu(A \cap B) \mu(A \cap B) \geq \mu(A) \mu(B) \quad (3.15)$$

for all $A, B \in \mathcal{P}(X)$ and f and g are both increasing (or both decreasing) functions on X , then

$$\langle fg \rangle - \langle f \rangle \langle g \rangle \geq 0. \quad (3.16)$$

The brackets denote averages with respect to the measure μ . When applied to an Ising system of spin- $\ell/2$ particles where the Hamiltonian is given by eqn.(3.8) with $J_{ij} \geq 0$ and no restriction on h_i , (3.15) holds and inequality (3.16) tells us that the second GKS inequality holds. The main point to note here is that the second GKS inequality holds for arbitrary external fields. Cartier⁽⁶⁶⁾, extended (3.16) to Ising spin particles whose spin measure is continuous.

A new inequality, now known as the GHS inequality appeared in the work of Griffiths, Hurst and Sherman⁽⁴⁸⁾. It is valid for the Hamiltonian given by eqn.(3.8) with $J_{ij} \geq 0$ and $h_i \geq 0$ and single-spin measure ν given by eqn.(3.2) for arbitrary ℓ . This inequality states that

$$u_3(i,j,k) \leq 0, \quad (3.17)$$

where $u_3(i,j,k)$ is the third Ursell function defined by

$$\begin{aligned} u_3(i,j,k) &= \frac{\partial^3}{\partial h_i \partial h_j \partial h_k} \log Z, \\ &= \langle \sigma_i \sigma_j \sigma_k \rangle - \langle \sigma_i \sigma_j \rangle \langle \sigma_k \rangle - \langle \sigma_i \sigma_k \rangle \langle \sigma_j \rangle \\ &\quad - \langle \sigma_j \sigma_k \rangle \langle \sigma_i \rangle + 2 \langle \sigma_i \rangle \langle \sigma_j \rangle \langle \sigma_k \rangle \end{aligned} \quad (3.18)$$

with

$$Z = \sum_{\sigma \in X} \exp \left\{ \frac{1}{\tau} \sum_{i \neq j} J_{ij} \sigma_i \sigma_j + \sum_i h_i \sigma_i \right\}. \quad (3.19)$$

The proof uses the method of Griffiths^(41,42,45) and Kelly and Sherman⁽⁶¹⁾. This inequality was used by Griffiths, Hurst and Sherman to prove the concavity of the magnetization in a positive external field.

More interesting developments on correlation inequalities were motivated by the work of Percus⁽⁵²⁾. These we discuss in the next section.

3 THE DUPLICATE VARIABLE METHOD AND CORRELATION INEQUALITIES FOR FERRORMAGNETIC ISING SPIN SYSTEMS

The duplicate variable method is a powerful technique for proving different correlation inequalities for Ising spin systems. The method has been used in a wide variety of situations but may be identified by its two characteristic features. The first (from where the method receives its name) consists in expressing the product of correlation functions as an average of a suitable function over a larger space. The second feature of the method consists in a change of variables chosen in such a way that the inequality we set out to prove appears more evidently. The method has been applied successfully to simplify the proofs and extend the correlation inequalities we mentioned in the last section to more general types of interactions and single-spin measures. It has also been applied to obtain new inequalities that will be discussed in this section.

We can explain more precisely the duplicate variable method. Suppose that for a generalised Ising-spin ferromagnet (Λ, H, ν) we want to prove that the n th order correlation function

$$\prod_{\alpha=1}^n \langle f_{\alpha}(\underline{q}) \rangle = Z^{-n} \prod_{\alpha=1}^n \int f_{\alpha}(\underline{q}) \exp(-H(\underline{q})) d\nu(\underline{q}) , \quad (3.20)$$

is non-negative, where f_{α} , $\alpha = 1, \dots, n$, are real valued functions defined over the configuration space. In this expression Z is given by Eq.(3.4) and $d\nu(\underline{q}) = \prod_{i=1}^N d\nu(\sigma_i)$, where ν is the single-spin measure. The first step of the method, consists in expressing (3.20) as an expectation over a large space. This is the space obtained by considering n copies of the original system, that is, X^n , where X is the configuration space of (Λ, H, ν) . Then, we may write

$$\begin{aligned} \prod_{\alpha=1}^n \langle f_{\alpha}(\underline{g}) \rangle &= \\ &= \bar{Z}^{-1} \int_{\mathbf{X}^n} \left[\prod_{\alpha=1}^n f_{\alpha}(\underline{g}^{(\alpha)}) \right] \exp \left[- \sum_{\alpha=1}^n H(\underline{g}^{(\alpha)}) \right] d\nu(\underline{g}^{(1)}, \dots, \underline{g}^{(n)}), \quad 3.21 \end{aligned}$$

where $\bar{Z} = Z^n$, $\underline{g}^{(\alpha)}$, $\alpha = 1, \dots, n$, denotes the spin configuration of the α th copy of the original system (Λ, H, ν) , and

$$d\nu(\underline{g}^{(1)}, \dots, \underline{g}^{(n)}) = \prod_{\alpha=1}^n d\nu(\underline{g}^{(\alpha)}).$$

The new system consists of n copies of the original model that do not interact with each other.

One way we can prove that (3.21) is non-negative is by proving that the integrand $\prod_{\alpha=1}^n f_{\alpha}(\underline{g}^{(\alpha)})$ is non-negative. In general, simple inspection of this term will not give us any information about its sign, so the next step of the method is to apply a suitable transformation (usually orthogonal)

$$s_i^{(\alpha)} = \sum_{\beta=1}^n A_{\alpha\beta} \sigma_i^{(\beta)} \quad (3.22)$$

such that in the new variables

$(\underline{s}^{(1)}, \dots, \underline{s}^{(n)}) = (s_1^{(1)}, \dots, s_N^{(1)}, \dots, s_1^{(n)}, \dots, s_N^{(n)})$ the integrand is more easily seen to be non-negative.

We will denote by A the matrix whose elements are given by $A_{\alpha,\beta}$, $\alpha, \beta = 1, \dots, n$, defined by Eq.(3.22).

The duplicate variable method was first identified as a distinct technique for proving correlation inequalities by Percus⁽⁵²⁾, although as we mentioned in the last section, Ginibre⁽⁶²⁾, used the basic ideas of the method to prove the second GKS inequality and Griffith⁽⁶³⁾, used the idea of adding another (although not identical) ferromagnetic system to the original one.

To prove the second GKS inequality which involves second-order correlations, Percus doubled the system and considered the change of variables given by (3.22) for the matrix

$$A^{(2)} = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}. \quad (3.23)$$

The original system is assumed to be a spin- $\frac{1}{2}$ Ising ferromagnet with Hamiltonian

$$H(\sigma) = -\frac{1}{2} \sum_{i \neq j} J_{ij} \sigma_i \sigma_j - \sum_i h_i \sigma_i \quad (3.24)$$

with non-negative interaction constants J_{ij} and arbitrary external fields h_i . The new variables $s_i^{(1)}, s_i^{(2)}$ defined by equations (3.22) and (3.23), $i = 1, \dots, N$ can take on the values $-1, 0$ and 1 with the constraint that $s_i^{(1)} = 0$ implies $s_i^{(2)} = \pm 1$ and $s_i^{(2)} = 0$ implies $s_i^{(1)} = \pm 1$.

With the help of the new variables we may write

$$\begin{aligned} w_{ij} &= \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \\ &= \frac{1}{Z} \int (\sigma_i^{(1)} - \sigma_i^{(2)}) (\sigma_j^{(1)} - \sigma_j^{(2)}) \exp[-H(\underline{\sigma}^{(1)}) - H(\underline{\sigma}^{(2)})] d\nu(\underline{\sigma}^{(1)}) d\nu(\underline{\sigma}^{(2)}) \\ &= \frac{1}{Z} \int s_i^{(1)} s_i^{(2)} \exp[-H(\underline{s}^{(1)}, \underline{s}^{(2)})] d\nu(\underline{s}^{(1)}, \underline{s}^{(2)}), \quad (3.25) \end{aligned}$$

where

$$Z = \int_{X^2} \exp[-H(\underline{s}^{(1)}, \underline{s}^{(2)})] dv(\underline{s}^{(1)}, \underline{s}^{(2)}) \quad (3.26)$$

and $H(\underline{s}^{(1)}, \underline{s}^{(2)})$ is the Hamiltonian of the doubled system expressed in the new variables. By using Eq. (3.23) in (3.22) we find that

$$H(\underline{s}^{(1)}, \underline{s}^{(2)}) = -\frac{1}{2} \sum_{i \neq j} 2J_{ij} [s_i^{(1)} s_j^{(1)} + s_i^{(2)} s_j^{(2)}] - \sum_i 2h_i s_i^{(1)}. \quad (3.27)$$

Again, using (3.22) and (3.23) we find that the measure appearing in Eq.(3.26) is given by

$$dv(\underline{s}^{(1)}, \underline{s}^{(2)}) = \prod_{i=1}^N dv(s_i^{(1)}, s_i^{(2)}),$$

where

$$dv(s_i^{(1)}, s_i^{(2)}) = dv(s_i^{(1)} - s_i^{(2)}) dv(s_i^{(1)} + s_i^{(2)}) = dv(\sigma_i^{(1)}) dv(\sigma_i^{(2)}).$$

Since $dv(\sigma_i^{(1)})$ is an even measure, one can easily verify that $dv(s_i^{(1)}, s_i^{(2)})$ is invariant under any change of sign of $s_i^{(1)}$ or $s_i^{(2)}$.

The proof given by Percus relies on the fact that thermal averages in the doubled system may be expressed as traces of suitable matrices and by showing that through the transformation given by (3.22) and (3.23) the matrix corresponding to $\exp[-H(\underline{s}^{(1)}, \underline{s}^{(2)})]$ has non-negative off-diagonal elements and that the matrix elements of $s_i^{(2)} s_j^{(2)}$ appearing in Eq.(3.25) are also non-negative. Instead of giving the proof of Percus, we shall exhibit a somewhat simpler proof due to Sylvester⁽⁶⁷⁾, which has the additional advantage of being valid for any even single-spin measure and not restricted to the spin- $\frac{1}{2}$ case.

From (3.25)-(3.27) we see that to prove that $W_{ij} \geq 0$ we have to prove that

$$\int s_i^{(2)} s_j^{(2)} \exp\left\{\frac{1}{2} \sum_{i \neq j} J_{ij} [s_i^{(1)} s_j^{(1)} + s_i^{(2)} s_j^{(2)}] + \sum_i 2h_i s_i^{(1)}\right\} d\nu(s^{(1)}, s^{(2)}) \geq 0. \quad (3.28)$$

The expansion in Taylor series of $\exp\left[\frac{1}{2} \sum_{i \neq j} J_{ij} s_i^{(2)} s_j^{(2)}\right]$ is a series with non-negative coefficients (since $J_{ij} \geq 0$) and so the integral of (3.28) can be written as a series whose terms have the form

$$\int \prod_{k=1}^N [s_k^{(2)}]^{m_k} \exp\left\{\frac{1}{2} \sum_{i \neq j} 2 J_{ij} s_i^{(1)} s_j^{(1)} + \sum_i 2 h_i s_i^{(1)}\right\} d\nu(s^{(1)}, s^{(2)}) \quad (3.29)$$

multiplied by non-negative coefficients. In this expression m_k , $k = 1, \dots, N$, are arbitrary non-negative integers. By the symmetry of the measure $d\nu(s^{(1)}, s^{(2)})$ the last integral vanishes unless all the m_k are even, in which case the integrand is positive. This proves that $W_{ij} \geq 0$.

Percus also proved the GHS inequality for spin- $\frac{1}{2}$ particles in an arbitrary external field. Since this inequality involves third-order correlation function it is necessary to consider three copies of the original system. This proof can also be found in the review paper of Cartier⁽⁶⁶⁾. By considering four copies the proof was further simplified and extended to more general single-spin measures^(67,68,69).

Lebowitz⁽⁷⁰⁾, used the duplicate variable method to prove a set of interesting correlation inequalities from which the GHS inequality may be extracted as a special case. The model is a spin- $\frac{1}{2}$ Ising ferromagnet with 2-body interactions and arbitrary external field, Eq. (3.24). Consider the system described by the spin- $\frac{1}{2}$ variables

$(\sigma^{(1)}, \sigma^{(2)}) = (\sigma_1^{(1)}, \dots, \sigma_N^{(1)}, \sigma_1^{(2)}, \dots, \sigma_N^{(2)})$ obtained by duplicating the original system and use the transformation (3.22) with $A^{(2)}$ given by (3.23) to define the new set of variables $(s^{(1)}, s^{(2)}) = (s_1^{(1)}, \dots, s_N^{(1)}, s_1^{(2)}, \dots, s_N^{(2)})$. That is,

$$\begin{aligned} s^{(1)} &= \frac{1}{2}[\sigma_i^{(1)} + \sigma_i^{(2)}] \\ s^{(2)} &= \frac{1}{2}[-\sigma_i^{(1)} + \sigma_i^{(2)}], \quad i \in \Lambda. \end{aligned} \quad (3.30)$$

Then, the Lebowitz inequalities are¹

$$\langle s_A^{(2)} \rangle \geq 0, \quad A \subset \Lambda; \quad (3.31)$$

$$\langle s_A^{(1)} s_B^{(2)} \rangle \leq \langle s_A^{(1)} \rangle \langle s_B^{(2)} \rangle, \quad (3.32)$$

for $h_i \geq 0$, $A, B \subset \Lambda$; and

$$\langle s_A^{(2)} s_B^{(2)} \rangle \geq \langle s_A^{(2)} \rangle \langle s_B^{(2)} \rangle, \quad (3.33)$$

$A, B \subset \Lambda$. In these expressions

$$s_C^{(\alpha)} = \prod_{i \in C} s_i^{(\alpha)}, \quad \alpha = 1, 2, C \subset \Lambda.$$

¹ The averages appearing in equation (3.31)-(3.33) are calculated in the doubled system with Hamiltonian given by Eq.(3.27) and partition function given by Eq.(3.26).

The GHS inequality states that $u_3(i,j,k) \leq 0$ where u_3 is the third Ursell function. In general the ℓ th Ursell function is defined by

$$u_\ell(i_1, \dots, i_\ell) = \frac{\partial^\ell}{\partial h_{i_1} \dots \partial h_{i_\ell}} \log Z$$

where

$$Z = \int \exp[-H(\underline{g})] d\nu(\underline{g})$$

with H given by Eq.(3.24). Then, we readily find (again the brackets denote averages over the doubled system) that

$$u_1(i) = \langle s_i^{(1)} \rangle, \quad (3.34)$$

$$u_2(i,j) = 2 \langle s_i^{(2)} s_j^{(2)} \rangle, \quad (3.35)$$

(this is just Eq.(3.25)),

$$u_3(i,j) = 4[\langle s_i^{(2)} s_j^{(2)} s_k^{(1)} \rangle - \langle s_i^{(2)} s_j^{(2)} \rangle \langle s_k^{(1)} \rangle], \quad (3.36)$$

$$u_4(i,j) = 8[\langle s_i^{(2)} s_j^{(2)} s_k^{(1)} s_\ell^{(1)} \rangle - \langle s_i^{(2)} s_j^{(2)} \rangle \langle s_k^{(1)} s_\ell^{(1)} \rangle] \\ - 2[u_3(i,j,k) \langle s_\ell^{(1)} \rangle + u_3(i,j,\ell) \langle s_k^{(1)} \rangle]. \quad (3.37)$$

By putting $B = \{i,j\}$ and $A = \{k\}$ in inequality (3.23) and using (3.36) the GHS inequality follows. On the other hand, if all the external fields are zero $\langle s_i^{(1)} \rangle$ vanishes for all $i \in \Lambda$ and by putting $A = \{k,\ell\}$ $B = \{i,j\}$ in (3.32) we obtain with the help of Eq.(3.37) that

$$u_4(i,j,k,\ell) \leq 0.$$

Lebowitz avoided the use of a third or a third and a fourth copy by

using exhaustively throughout the proof the second GKS and the FK— inequalities.

Again, the method was used by Sylvester⁽⁶⁸⁾ to give a unified proof that the second, fourth and sixth Ursell functions at zero external field are non-negative, non-positive and non-negative respectively. The proof is valid for the Hamiltonian given by Eq.(3.24) with ferromagnetic interactions and zero external field and with single-spin measure given by (3.2) with $\ell = 1$. As Kelly and Sherman⁽⁵⁹⁾, showed the GHS inequality follows as a corollary from the fact that the fourth Ursell function at zero external field is non-positive.

Sylvester⁽⁶⁷⁾ presented an interesting review of correlation inequalities and gave some extensions using the duplicate variable method. In this paper the first and second GKS inequalities in the form given by (3.10) and (3.11) were proved for the general Ising spin system with Hamiltonian given by (3.1) ($J_A \geq 0$) and arbitrary even single-spin measure. The Lebowitz inequalities (3.31) - (3.33) were also extended to the Hamiltonian (3.24) with ferromagnetic interactions, and positive external field, and for the single-spin measure ν given by

$$d\nu(\sigma_i) = \frac{\exp[-P(\sigma_i)]d\sigma_i}{\exp[-P(\sigma_i)]d\sigma_i} \quad \forall i \in \Lambda, \quad (3.38)$$

where P is an even polynomial whose leading coefficient is positive, whose quadratic and constant coefficients are arbitrary and whose remaining coefficients are non-negative. These conditions have no physical meaning, they appear because the proof given by Sylvester requires that a

certain polynomial be non-negative. The proofs given by Sylvester are similar to that of the second GKS inequality $W_{ij} \geq 0$ given above.

The GKS and GHS inequalities were again investigated by the duplicate variable method by Ellis⁽⁷¹⁾ and Ellis, Monroe and Newman⁽⁶⁹⁾. The method is very similar to that employed by Sylvester. However, the main purpose here is to find the most general single-spin measure that will guarantee (3.17). The Hamiltonian is taken to be that of (3.24) with ferromagnetic interactions and positive external field. The GHS and GKS inequalities are proven in a unified way by using independent identically distributed copies of the original spin variables (one for the first GKS inequality, two for the second GKS inequality, four for the GHS inequality).

The matrix used to define the new set of variables is given by

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix},$$

for the proof of the second GKS inequality, and by the tensor product of the above matrix with itself to prove the GHS inequality. Their main result is the further extension of the set of single-spin measures for which the GHS inequality holds. It is established that the polynomial P appearing in Eq.(3.38) need only be an even differentiable function whose derivative is convex in $[0, \infty)$.

In a somewhat different form the method appeared in the work of Monroe and Siegert⁽⁷²⁾, Monroe⁽⁷³⁾, and Ellis and Monroe⁽⁷⁴⁾. Simple proofs of the GKS inequalities, certain FKG inequalities, the GHS inequality and other correlation inequalities are proved for a spin- $\frac{1}{2}$ system with ferromagnetic pair interactions and non-negative external fields.

The proofs are based on the identity⁽⁷⁵⁾

$$\exp\left[\frac{1}{2} \sum_{i,j} \zeta_i v_{ij} \zeta_j\right] =$$

$$(2\pi)^{-N/2} (\det v)^{\frac{1}{2}} \int \prod_{i=1}^N dx_i \exp \left[-\frac{1}{2} \sum_{i,j} x_i (v^{-1})_{i,j} x_j + \sum_i \zeta_i x_i \right]$$

(3.39)

valid for any symmetric, real, positive definite matrix v and for any N complex variable ζ_i . This identity is used by identifying the variables ζ_i with the spin- $\frac{1}{2}$ variables σ_i and forming the matrix $v = J$ with off-diagonal elements J_{ij} and diagonal elements $J_0 \equiv J_{ii}$ large enough to guarantee that J is positive definite. Then, the spin- $\frac{1}{2}$ variables σ_i are replaced by the continuous variables x_i and from this point on, the proof proceeds similarly to that of Sylvester⁽⁶⁷⁾, using two copies of the system to prove the second GKS inequality and certain FK G inequalities, and four copies to prove the GHS and other related correlation inequalities. In the first case a change of variables is effected with the help of the matrix

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

and in the second with the help of the tensor product of the above matrix with itself. The only drawback of their method is that it is valid only for spin- $\frac{1}{2}$ Ising particles. The same ideas (in particular Eq.(3.35)) were used by Monroe⁽⁷⁶⁾, to prove certain correlation inequalities for the plane rotator model.

The duplicate variable technique has also been used to prove more specialized correlation inequalities. van Beijeren⁽⁴⁷⁾, used it to simplify and improve Dobrushin's⁽⁷⁷⁾, result on the existence of a non-translational invariant state at sufficiently low temperatures for the three-dimensional nearest-neighbour Ising ferromagnet. van Beijeren proved the existence of a sharp interface at least up to the critical temperature of the corresponding two-dimensional system. We consider a simple cubic lattice on a cube of $2N + 1$ horizontal layers numbered $-N, -N+1, \dots, 0, \dots, N$. The spins on the layer 0 are denoted by $\sigma_\ell, \sigma_m, \sigma_n, \dots$, those on the layers ℓ, \dots, N by $\sigma_i, \sigma_j, \sigma_k, \dots$ and those on the layers $-1, \dots, -N$ by $\sigma_{-i}, \sigma_{-j}, \sigma_{-k}, \dots$ where the indexing is chosen in such a way that the sites i and $-i$ are symmetric with respect to the layer 0. We also consider a two dimensional square lattice of $(2N+1) \times (2N+1)$ sites whose spins we denote by $\sigma'_\ell, \sigma'_m, \sigma'_n, \dots$. The Hamiltonians of both systems are respectively given by

$$H(q) = J \left\{ \sum_{[ij]} (\sigma_i \sigma_j + \sigma_{-i} \sigma_{-j}) + \sum_{[mn]} \sigma_m \sigma_n + \sum_{[im]} \sigma_m (\sigma_i + \sigma_{-i}) \right\} \\ + \sum_i h_i (\sigma_i - \sigma_{-i}) + \sum_m H_m \sigma_m, \quad (3.40)$$

$$H'(q') = J \sum_{[mn]} \sigma'_m \sigma'_n + \sum_m H_m \sigma'_m. \quad (3.41)$$

The square brackets denote summation of pairs of nearest neighbours and we require that $J \geq 0$, $h_i, H_m \geq 0$. We now introduce the variables $s_i^{(1)}, s_j^{(1)}, \dots, s_m^{(1)}, s_n^{(1)}, \dots, s_i^{(2)}, s_j^{(2)}, \dots, s_m^{(2)}, s_n^{(2)}$ by the transformations

$$s_i^{(1)} = \frac{1}{2}(\sigma_i + \sigma_{-i}) \quad s_i^{(2)} = \frac{1}{2}(\sigma_i - \sigma_{-i}) \\ s_m^{(1)} = \frac{1}{2}(\sigma_m + \sigma'_m) \quad s_m^{(2)} = \frac{1}{2}(\sigma_m - \sigma'_m) \quad (3.42)$$

With this notation, using the duplicate variable method in the manner used by Lebowitz⁽⁷⁰⁾, van Beijeren proved that

$$\langle s_\ell^{(2)} \rangle \geq 0, \quad (3.43)$$

which, with the help of (3.42), tells us that $\langle \sigma_\ell \rangle \geq \langle \sigma'_\ell \rangle$. The last inequality tells us that the average magnetization of the central layer is larger than the average magnetization in a corresponding two-dimensional Ising system. We now give a simple proof, following the method as used by Sylvester⁽⁶⁷⁾ of inequality (3.43). The proof has the merit of applying to arbitrary even single-spin measures.

By using (3.42) we first note that the Hamiltonian of the doubled system may be written as

$$\begin{aligned} H(s_\ell^{(1)}, s_\ell^{(2)}) = & -2J \left[\sum_{[ij]} (s_i^{(1)} s_j^{(1)} + s_i^{(2)} s_j^{(2)}) + \sum_{[mn]} (s_m^{(1)} s_n^{(1)} + s_m^{(2)} s_n^{(2)}) \right. \\ & \left. + \sum_{[im]} (s_i^{(1)} s_m^{(1)} + s_i^{(1)} s_m^{(2)}) \right] - \sum_i 2h_i s_i^{(2)} - \sum_m 2H_m s_m^{(1)}. \end{aligned} \quad (3.44)$$

Then

$$\begin{aligned} \langle s_\ell^{(2)} \rangle = & \bar{Z}^{-1} \int s_\ell^{(2)} \exp \{ 2J \left[\sum_{[mn]} s_m^{(2)} s_n^{(2)} + s_i^{(1)} s_m^{(2)} \right] \} \\ & \times \exp \{ 2J \left[\sum_{[ij]} (s_i^{(1)} s_j^{(1)} + s_i^{(2)} s_j^{(2)}) + \sum_{[mn]} s_m^{(1)} s_n^{(1)} + \sum_{[im]} s_i^{(1)} s_m^{(1)} \right] + \right. \\ & \left. \sum_i 2h_i s_i^{(2)} + \sum_m H_m s_m^{(1)} \right\} \times \pi dv(s_i^{(1)}, s_i^{(2)}) dv(s_m^{(1)}, s_m^{(2)}), \end{aligned} \quad (3.45)$$

where \bar{Z} is the partition function of the doubled system and

$dv(s_i^{(1)}, s_i^{(2)}) = dv(\sigma_i^{(1)}) dv(\sigma_i^{(2)})$ and similarly for $dv(s_m^{(1)}, s_m^{(2)})$.

The first exponential appearing in (3.45) can be expanded in a Taylor series in the variables $s_i^{(1)}$ and $s_m^{(2)}$ with non-negative coefficients. Hence the integral appearing in (3.45) can be written as a series of terms of the form

$$\int \prod_k \prod_l (s_k^{(1)})^{n_k} (s_l^{(2)})^{n_l} \exp\{2J \sum_{[ij]} (s_i^{(1)} s_j^{(1)} + s_i^{(2)} s_j^{(2)}) + \sum_{[mn]} s_m^{(1)} s_n^{(1)} + \sum_{[im]} s_i^{(1)} s_m^{(1)} + \sum_i 2h_i s_i^{(2)} + \sum_m H_m s_m^{(1)}\} \prod dv(s_i^{(1)} s_i^{(2)}) \prod dv(s_m^{(1)} s_m^{(2)}),$$

multiplied by non-negative coefficients. The exponents n_k and n_l are non-negative arbitrary integers. By symmetry this last integral vanishes unless all the exponents n_i and n_m are even, in which case the integral is non-negative. Hence, inequality (3.43) is proved.

To prove the existence of a sharp interface in the three-dimensional system at least up to the critical temperature of the two-dimensional system we consider the case where all the h_i and H_m are $+\infty$ at the boundary sites and zero at all other sites. We can obtain a system of $2N$ layers from the $2N+1$ layer system in the following way: start with the $2N+1$ layer system with external magnetic fields as specified above and apply an infinite positive field to all spins in the layers $N-1$. This leaves us with a $2N$ layer system, antisymmetric with respect to the plane between the layers 0 and 1. By the second GKS inequality it follows that the average magnetization of the 0 layer is not decreased by increasing the fields of the $N-1$ layer, hence, by inequality (3.43), in this new system the average magnetization of the layer 0 is still larger than the average magnetization in the corresponding two-dimensional Ising system.

By symmetry the average magnetization in the layer -1 is exactly the opposite of that in the layer 0 . We finally conclude that under the given boundary conditions there is indeed a sharp interface between the layers 0 and -1 . The proof obviously carries through for more general interactions provided there is no interaction between the top layers and the lower ones and that the symmetry is maintained.

When applied to a two-dimensional nearest-neighbour Ising ferromagnet, van Beijeren's method gives us no information on the existence of non-translational invariant states since the critical temperature of the corresponding one-dimensional system is zero. On the other hand, Gallavotti⁽⁷⁸⁾ and Abraham and Reed^(79,80) showed that in two dimensions the interface is diffuse, its width being of the order of the square of its length. This suggests the non-existence of non-translational invariant states in two dimensions, although a rigorous proof is still lacking. Messager and Miracle-Sole⁽⁸¹⁾ proved that for a large class of boundary conditions the equilibrium state of a two-dimensional nearest-neighbour Ising ferromagnet is translationally invariant, hence making very unlikely the existence of non-translational invariant states. They also presented some other results on further topics. The proofs use the duplicate variable method in an ingenious way by combining half of the system with the other. We now give a brief description of how they used the method.

Consider for simplicity a simple cubic lattice Z^2 and a cubic box Λ in the lattice. A lattice site $i \in \Lambda$ may be represented by its coordinates $i = (i_1, i_2)$. The Hamiltonian of the system is given by

$$H(\sigma) = -J \sum_{[ij] \subset \Lambda} \sigma_i \sigma_j - \sum_{i \in \Lambda} h_i \sigma_i, \quad (3.46)$$

where the square brackets denote summation over nearest neighbour pairs and of course $J \geq 0$. The second sum represents the action of an external field and/or boundary term. In the latter case we take

$$h_i = Jb_i, \quad b_i \pm 1$$

for i in the boundary of Λ . Now, let Λ be symmetric with respect to the line to the line $i_1 = -1/2$ and for any site $i \in \Lambda$ let i' denote the reflection of this site with respect to the line $i_1 = -1/2$. For any boundary conditions satisfying $b_i + b_{i'} \geq 0$ (or alternatively $b_i + b_{i'} \leq 0$) for all $i \in \Lambda$, Messager and Miracle-Sole proved that the equilibrium state is translationally invariant and furthermore, that it is a convex combination of the equilibrium states for (+) and (-) boundary conditions. Besides using the duplicate variable method, the proof also relies on the FKG inequalities and other correlation inequalities recently obtained by Lebowitz⁽⁸²⁾. We will give an idea of how the method of duplicate variables was used by Messager and Miracle by proving that

$$\langle \sigma_{(0,0)} \sigma_{(m,n)} \rangle \geq \langle \sigma_{(0,0)} \sigma_{(m+1,n)} \rangle \quad (3.47)$$

if $m \geq 0$, $n \geq 0$, and the external field is uniform and non-negative. This inequality was also proved by Messager and Miracle-Sole. Inequality (3.47) proves the decrease with distance of the two-point correlation function. It is valid for an Ising ferrormagnet in any number of dimensions, in which case the subindices in (3.47) indicate the first two coordinates of the lattice, the other coordinates being equal.

Instead of duplicating the system and then combining it by means of some transformation, Messenger and Miracle-Sole combined half of the system with the other half by introducing new variables $s_i^{(1)}, s_i^{(2)}$, $i \in \Lambda_1$ (Λ_1 is the part of Λ where $i_1 \geq 0$) through the transformations

$$s_i^{(1)} = \frac{1}{2}(\sigma_i + \sigma_{i'}) \quad (3.48)$$

$$s_i^{(2)} = \frac{1}{2}(\sigma_i - \sigma_{i'}).$$

In the new variables, the Hamiltonian (3.46) is

$$\begin{aligned} H(s^{(1)}, s^{(2)}) = & -2J \left\{ \sum_{[ij] \subset \Lambda} (s_i^{(1)} s_j^{(1)} + s_i^{(2)} s_j^{(2)}) \right. \\ & \left. - J \sum_{\substack{i \in \Lambda_1 \\ i_1=0}} (2(s_i^{(1)})^2 - 1) + \sum_{i \in \Lambda_1} H_i s_i^{(1)} + K_i s_i^{(2)} \right\}, \end{aligned} \quad (3.49)$$

where

$$H_i = h_i - h_{i'}, \quad K_i = h_i + h_{i'}.$$

Now

$$\langle s_i^{(2)} s_j^{(2)} \rangle = Z^{-1} \int s_i^{(2)} s_j^{(2)} \exp[-H(s^{(1)}, s^{(2)})] dv(s^{(1)}, s^{(2)}). \quad (3.50)$$

By hypothesis $H_i = H = 0$ and $K_i = 2h \geq 0$. Hence the exponential appearing in the integral above can be expanded in a series with non-negative coefficients which means that the integral above may be written as a series of integrals of the form

$$\int \prod_k \prod_l (s_k^{(1)})^{m_k} (s_l^{(2)})^{m_l} dv(s^{(1)}, s^{(2)})$$

multiplied by non-negative coefficients. In this expression m_k and m_l are non-negative coefficients. For any even single-spin measure ν the above integral vanishes unless all the exponents are even, in which case the integrand is non-negative. Hence,

$$\langle s_i^{(2)} s_j^{(2)} \rangle \geq 0, \quad (3.51)$$

which is analogous to the Lebowitz inequality, Eq. (3.31). From this inequality, the symmetry of Λ and $H(l)$ and putting $i=(-m-1, -n)$, $j=(-1, 0)$ in (3.51), inequality (3.47) follows.

Messenger, Miracle-Sole and Pfister⁽⁸⁴⁾ applied the method to prove some correlation inequalities for the plane rotator model which are analogous to some correlation inequalities obtained by Lebowitz⁽⁸²⁾. The method is applied in the general way mentioned above. With the help of these inequalities it may be proved that if the model is isotopic (rotation invariant) and the free energy is a continuously differentiable function of the external field h , then there is a unique translational invariant Gibbs state, and if $h=0$ all Gibbs states are invariant by rotation of the spins.

In what we have discussed so far, once the system is duplicated the transformation used to combine both systems is given by a simple matrix, as the one given by Eq. (3.23). However, the choice of such a transformation is arbitrary as long as the problem is solved, and in particular, the transformation used might even be non-linear. Dunlop⁽⁸³⁾ considered an Ising spin- $\frac{1}{2}$ ferromagnet with pair interactions and arbitrary (complex) external field h . For this system he proved a set of correlation inequalities which in turn allowed him to prove that the pressure is an analytic function of the external field for $|\text{Im } h| < \text{Re } h$. Without going into the details of the proof, the inequalities follow from duplicating

the system and introducing new variables n_i , $i = 1, \dots, N$, by the transformation

$$\begin{aligned}\cos(\tfrac{1}{2}n_i\pi) &= \tfrac{1}{2}(\sigma_i^{(1)} + \sigma_i^{(2)}) \\ \sin(\tfrac{1}{2}n_i\pi) &= \tfrac{1}{2}(\sigma_i^{(1)} - \sigma_i^{(2)})\end{aligned}\tag{3.53}$$

where $n_i = 0, 1, 2, 3$ according to the values of $\sigma_i^{(1)}$ and $\sigma_i^{(2)}$. Hence, averages over the configuration space of the doubled system are transformed into averages over the space $\{0, 1, 2, 3\}^N$, and the proof of the correlation inequalities mentioned above follows from showing that in the new variables the required averages have the desired positivity properties.

We end this section with a brief mention of the application of the method in the plane rotator model. This model is a generalization of the Ising spin system in the sense that the spin variables are now two-dimensional variables. That is, with each site we associate a two-dimensional spin vector $\vec{\sigma}_i = (s_i, t_i)$ where s_i and t_i denote real numbers. In order to prove correlation inequalities for this system using the method the variables s_i and t_i are treated separately. That is, once the system is duplicated the variables s_i of both systems are combined by a transformation that is usually of the form given by Eq. (3.22) while the variables t_i of both systems are combined by another transformation. Messager, Miracle-Sole and Pfister⁽⁸⁴⁾ proved some correlation inequalities which enabled them to prove that if the free energy is a continuously differentiable function of the external field, there is a unique invariant state. With the help of similar correlation inequalities Bricmont, Fontaine and Landau⁽⁸⁵⁾ proved the existence of a unique translation invariant state in zero external field if there is no spontaneous magnetization.

4. CONCLUSIONS

The duplicate variable method is a useful tool for proving correlation inequalities. As we have seen the method permits one to prove correlation inequalities in a simple way and extend them to more general interactions and/or single-spin measures. The method applies best when the system is duplicated at every step, i.e., from one copy we pass to two to prove inequalities involving second-order correlation functions, and then to four copies (not three) to prove inequalities involving third and fourth order correlation functions. However, a third duplication (eight copies of the original system) has yet found no application.

The idea of combining the system with itself as was done by van Beijeren⁽⁴⁷⁾ and Messenger and Miracle-Sole⁽⁸¹⁾, is an interesting development of the method. In order that the method be applied in this form it is necessary to introduce a symmetry in the system. This has the drawback that the symmetry appears in the results. Thus, in van Beijeren's work this means that although the results apply for more general interactions than nearest-neighbors, the spins on the top layers may not interact with those below. In the work of Messenger and Miracle-Sole the class of boundary conditions for which no non-translational invariant state exists is defined in terms of the line of symmetry of the lattice. It seems then that in order to rule out the possibility of non-translational invariant states in two dimensions, some other method must be employed, although it might be possible to extend further the class of boundary conditions for which no non-translational invariant states exist by considering other lines of symmetry of the lattice.

The method has also been applied to other models and in this direction much work remains to be done. The method has been particularly useful in proving correlation inequalities for the plane rotator model^(76,81,84,85) and might be used to extend the results of van Beijeren⁽⁴⁷⁾ and Messenger and Miracle-Sole⁽⁸¹⁾ for the Ising ferromagnet to the plane rotator model, although it is more difficult to take into account the boundary conditions in the latter.

APPENDIX A. CONVEX FUNCTIONS AND GENERALIZED LEGENDRE TRANSFORMS

The concepts of convex functions and generalized Legendre transforms arise naturally in the rigorous discussions of statistical mechanics and in the problem of the thermodynamic equivalence of ensembles. Generalized Legendre transforms have striking properties when applied to convex (or concave) functions. Those relevant to our problem are stated in this appendix, following Fenchel⁽²⁴⁾, Rockafellar^(25,26) and Roberts and Varberg⁽²⁷⁾. Legendre transforms are also defined. They can be applied under more restrictive conditions than generalized Legendre transforms, however, as theorem A.5 below shows, they are equivalent for convex functions when they can be applied.

We start by introducing the definitions of convex function and of Legendre and generalized Legendre transform.

DEFN. A.1

- (a) Let G be a subset of \mathbb{R}^n . We say that G is convex if for every pair of points $x, x' \in G$, $\alpha x + (1-\alpha)x' \in G$ for any $\alpha \in [0,1]$.
- (b) Let $G \subset \mathbb{R}^n$ be a convex set. The function $f : G \rightarrow \mathbb{R}$ is convex if

$$f(\alpha x + (1-\alpha)x') \leq \alpha f(x) + (1-\alpha)f(x') \quad (\text{A.1})$$

for any pair of points $x, x' \in G$ and any $\alpha \in [0,1]$. We say that f is strictly convex if strict inequality holds in (A.1) for every pair of points $x, x' \in G$ and any $\alpha \in [0,1]$.

- (c) We say that $f : G \rightarrow \mathbb{R}$ with G a convex subset of \mathbb{R}^n is concave (strictly concave) if $-f$ is convex (strictly convex).

In what follows, we work only with convex functions; all our results and definitions will apply, with obvious modifications, to concave functions.

A convex function is continuous and is differentiable, except, at most, on a countable number of points. If G is a convex subset of R , the condition that $f : G \rightarrow R$ be convex can be stated geometrically by saying that for every pair of points $x, x' \in G$, each point of the chord between $(x, f(x))$ and $(x', f(x'))$ does not lie below the graph of f .

DEFN. A.2

Let $G \subset R^n$ be a convex set, and let $f : G \rightarrow R$ be a convex function. The generalized Legendre transform of f (also known as the conjugate convex function of the convex function f) is defined as the function $f^* : G^* \rightarrow R$ where

$$f^*(y) = \sup_{x \in G} [\sum x_i y_i - f(x)] \quad (A.2)$$

and $G^* \subset R^n$ is the set of all points $y = (y_1, \dots, y_n)$ for which $\sum x_i y_i$ is bounded above.

DEFN. A.3

Let G be a convex subset of R^n . Let $f : G \rightarrow R$ be a convex function whose second total derivative is continuous in G . Let

$$(y_1, \dots, y_n) = \left(\frac{\partial f}{\partial x_1}, \dots, \frac{\partial f}{\partial x_n} \right)$$

be the first derivative of f , so that $y_i = y_i(x_1, \dots, x_n)$ for

each $i = 1, \dots, n$, or more concisely, $y = y(x)$. If the determinant of the Hessian matrix of f is non-zero, $y = y(x)$ may be inverted to get $x = x(y)$. Then, the function \tilde{f} defined by

$$\tilde{f}(y) = \sum x_i y_i - f(x(y)) \quad (\text{A.3})$$

is known as the Legendre transform of f .

A Legendre or generalized Legendre transform may be applied to functions which are not necessarily convex. However, as the following theorem shows, it is when applied to convex functions, that they exhibit interesting properties. We also remark that they may be applied in some of the n variables of the function f .

As can be seen from defn. A.3 the conditions under which the Legendre transform may be applied are rather restricted, requiring in particular the continuity of the first and second order partial derivatives. If the function we want to apply the Legendre transform is, for example, the entropy density or the Gibbs free energy density, some of these conditions may not be met when phase transitions are present. Hence, we replace Legendre transforms by generalized Legendre transforms whenever we want to discuss phase transitions. Theorem A.5 establishes the equivalence of Legendre and generalized Legendre transforms whenever they can be defined. Before stating this theorem, we introduce the concept of a closed convex function and of a generalized derivative of a convex function.

DEFN A.4

Let G be a convex subset of R^n and $f : G \rightarrow R$ a convex function

- (a) We say that f is closed if the set $L_\beta = \{x \in G : f(x) \leq \beta\}$ is a closed subset of G for each real β .
- (b) A hyperplane of support of $z = f(x)$ at $x^{(0)} = (x_1^{(0)}, \dots, x_n^{(0)})$ is a hyperplane that touches the graph of f at $(x^{(0)}, f(x^{(0)}))$ but lies nowhere above the graph of f .

That is the hyperplane $z = \sum x_i y_i + b$ with normal vector $(y_1, \dots, y_n, -1)$ and z -intercept b is a hyperplane of support of f at $x^{(0)}$ if

$$f(x^{(0)}) = \sum x_i^{(0)} y_i + b$$

and

$$f(x) \geq \sum x_i y_i + b.$$

The generalized derivative or subdifferential ∂f of the function f is the set valued function defined by

$$\partial f(x) = \{y = (y_1, \dots, y_n) : (y_1, \dots, y_n, -1) \text{ is the normal vector of a hyperplane of support of } f \text{ at } x\}.$$

The closedness of a convex function f is related to its behavior on the boundary of G . The generalized derivative of f agrees with the total derivative of f wherever the latter is defined.

THM A.5

Let G be a convex subset of \mathbb{R}^n and $f : G \rightarrow \mathbb{R}$ a convex closed function. Then

- (i) $f^* : G \rightarrow \mathbb{R}$ is also convex and closed.
- (ii) $\sum x_i y_i \leq f(x) + f^*(y)$ for all $x \in G$, for all $y \in G^*$.
- (iii) $\sum x_i y_i = f(x) + f^*(y)$ if and only if $y \in \partial f(x)$.
- (iv) $\partial(f^*) = (\partial f)^{-1}$.⁶

Assume that $f : G \rightarrow \mathbb{R}$ is such that the Legendre transform \tilde{f} of f may be defined. Then (iii) of thm. A.5 tells us that

$$f^* = \tilde{f}, \tag{A.4}$$

which proves the equivalence of the Legendre and generalized Legendre transforms. Statement (iv) tells us how the generalized derivatives of f and f^* are related, for example, if f has a continuous derivative, f^* also has a continuous derivative. Statement (v) shows that in some sense f^* is the dual of f .

⁶ As a simple example, consider the case where $G \subset \mathbb{R}$. Then the graph of the subdifferential ∂f of f coincides with the graph of the derivative of f wherever it is defined. Wherever the derivative has a jump discontinuity, the graph of ∂f consists of a vertical line that bridges the jump. Then, $(\partial f)^{-1}$ is the set-valued function whose graph is the reflection of the graph of ∂f with respect to the line that passes through the origin with slope 1.

APPENDIX B. A SUMMARY OF THERMODYNAMICS

We present a brief summary of the formalism of thermodynamics in order that the problem of the thermodynamic equivalence of ensembles be better appreciated. We follow closely the classical work of Callen⁽²⁸⁾, which is appropriate enough for our purpose. In particular, we present the definition of the thermodynamic potentials which we treat explicitly. As mentioned in Appendix A, the entropy density $s = s(\epsilon, \rho)$ must satisfy certain restrictive conditions in order that its Legendre transform be well defined. These restrictions turn out to be incompatible with the existence of some phase transitions. Since we would like the formalism to allow for these, we are led to redefine the thermodynamic potentials. This we do with the help of the appropriate generalized Legendre transform.

Callen's postulates are:

- I - There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy E , the volume V , and the number of particles N .
- II - There exists a function (called the entropy S) of E, N, V , $S = S(E, N, V)$ defined for all equilibrium states. The entropy has the following property: the values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.
- III - The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

The fourth postulate proposed by Callen is the third law of thermodynamics which is not relevant to our discussion.

The temperature T (or inverse temperature β), the chemical potential μ and the pressure p are defined by

$$\frac{1}{T} = \beta = \left(\frac{\partial S}{\partial E} \right)_{N,V}$$

$$\bar{\mu} = -\frac{1}{\beta} \left(\frac{\partial S}{\partial N} \right)_{E,V}$$

$$p = \frac{1}{\beta} \left(\frac{\partial S}{\partial V} \right)_{E,N}$$

The relation $S = S(E, N, V)$ is known as a fundamental relation because all conceivable thermodynamic information may be obtained from it. The third postulate implies that the entropy is a homogeneous first order function of the variables E, N, V . Hence, the entropy density $s = s(\epsilon, \rho)$ where $s = SV^{-1}$, $\epsilon = EV^{-1}$ and $\rho = nV^{-1}$ is also a fundamental relation. ϵ and ρ are known as the energy and number density respectively. In what follows, we work with $s = s(\epsilon, \rho)$, because it is in this form that the entropy arises naturally in the problem of the thermodynamic equivalence of ensembles.

With the help of Legendre transforms, the fundamental relation $s = s(\epsilon, \rho)$ may be transformed into another one where the independent variables are the inverse temperature β and the number density ρ , or another one where the independent variables are the inverse temperature β and the chemical potential μ . These two fundamental relations are taken conventionally as the Helmholtz free energy density $\bar{f} = \bar{f}(\beta, \rho)$ and the pressure $\bar{p} = \bar{p}(\beta, \bar{\mu})$ defined by

$$\beta \bar{f}(\beta, \rho) = \beta \epsilon - s(\epsilon, \rho) \quad (A.1)$$

and

$$\begin{aligned} -\beta \bar{p}(\beta, \bar{\mu}) &= \beta \epsilon - \bar{\mu} \beta \rho - s(\epsilon, \rho) \\ &= -\bar{\mu} \beta \rho - s(\epsilon, \rho). \end{aligned} \quad (A.2)$$

When discussing phase transitions, the definitions introduced above may be wrong. For example, during the solid-liquid phase transition of water, energy is applied to the system while the temperature remains constant. Hence,

$$\frac{\partial^2 s}{\partial \epsilon^2} = \frac{\partial \beta}{\partial \epsilon} = 0,$$

and according to defn A.3 $\bar{f} = \bar{f}(\beta, \rho)$ cannot be defined.

To overcome these kinds of difficulties we use generalized Legendre transforms, keeping in mind relation (A.4). That is, we redefine the Helmholtz free energy density $\bar{f} = \bar{f}(\beta, \rho)$ and the pressure $\bar{p} = \bar{p}(\beta, \bar{\mu})$ by

$$\beta \bar{f}(\beta, \rho) = \inf_{\epsilon} [\beta \epsilon - s(\epsilon, \rho)].$$

$$\text{or} \quad \bar{f}(\beta, \rho) = \inf_{\epsilon} [\epsilon - \beta^{-1} s(\epsilon, \rho)], \quad (B.3)$$

$$\text{and} \quad -\beta \bar{p}(\beta, \bar{\mu}) = \inf_{\rho} \inf_{\epsilon} [\beta \epsilon - \bar{\mu} \beta \rho - s(\epsilon, \rho)],$$

$$\text{or} \quad \bar{p}(\beta, \bar{\mu}) = - \inf_{\rho} \inf_{\epsilon} [\epsilon - \bar{\mu} \rho - \beta^{-1} s(\epsilon, \rho)]$$

$$= - \inf_{\rho} [-\bar{\mu}\rho + \bar{f}(\beta, \rho)]$$

$$= \sup_{\rho} [\bar{\mu}\rho - \bar{f}(\beta, \rho)].^7 \quad (\text{B.4})$$

7 The generalised Legendre transform of a concave function is defined similarly to that of a convex function, replacing the supremum by an infimum.

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